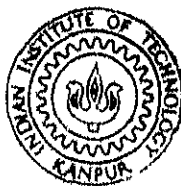


PHOTOCHEMICAL INVESTIGATIONS OF SELECTED ORGANIC
SUBSTRATES CONTAINING 1,2-DIBENZOYLALKENE
MOIETIES AND RELATED SYSTEMS

by
R. BARIK



TH
CHM/1986/D
B 239p

DEPARTMENT OF CHEMISTRY
INDIAN INSTITUTE OF TECHNOLOGY KANPUR
NOVEMBER, 1986

CHM
1986
D
BAR
PHO

✓
PHOTOCHEMICAL INVESTIGATIONS OF SELECTED ORGANIC
SUBSTRATES CONTAINING 1,2-DIBENZOYLALKENE
MOIETIES AND RELATED SYSTEMS

A Thesis Submitted
in Partial Fulfilment of the Requirements
for the Degree of
DOCTOR OF PHILOSOPHY

by
R. BARIK

to the

DEPARTMENT OF CHEMISTRY
INDIAN INSTITUTE OF TECHNOLOGY KANPUR
NOVEMBER, 1986

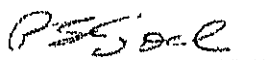
DEPARTMENT OF CHEMISTRY
INDIAN INSTITUTE OF TECHNOLOGY, KANPUR, INDIA

CERTIFICATE OF COURSE WORK

This is to certify that Mr. Rabindra Barik has satisfactorily completed all the courses required for the Ph.D. degree programme. These courses include:

Chm 500 Mathematics for Chemists I
Chm 502 Advanced Organic Chemistry II
Chm 511 Physical Organic Chemistry
Chm 524 Physical Methods in Chemistry
Chm 525 Principles of Physical Chemistry
Chm 608 Organic Photochemistry
Chm 800 General Seminars
Chm 801 Special Seminars
Chm 900 Post-Graduate Research

Mr. Rabindra Barik has successfully completed his Ph.D. Qualifying Examination in January 1983.



(P.S. Goel)

Head,
Department of Chemistry
IIT-Kanpur



(S. Sarkar)

Convener,
Departmental Post-
Graduate Committee,
Deptt. of Chemistry,
IIT-Kanpur

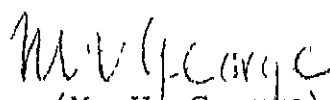
TO
MY PARENTS

21 DEC 1967

MINISTRY OF DEFENSE
1.1.1.1
Doc. No. 99213

CERTIFICATE II

Certified that the work embodied in this thesis entitled:
"Photochemical Investigations of Selected Organic Substrates
Containing 1,2-Dibenzoylalkene Moieties and Related Systems"
has been carried out by Mr. Rabindra Barik under my supervision
and the same has not been submitted elsewhere for a degree.


(M. V. George)
Thesis Supervisor

STATEMENT

I hereby declare that the matter embodied in this thesis is the result of investigations carried out by me in the Department of Chemistry, Indian Institute of Technology, Kanpur, India, under the supervision of Professor M.V. George.

In keeping with the general practice of reporting scientific observations, due acknowledgements have been made wherever the work described is based on the findings of other investigators.

R. Barik
R. Barik

ACKNOWLEDGEMENTS

It is with pleasure that I express my appreciation to Professor M. V. George for suggesting me the research problem embodied in this thesis and for supervising my work to a satisfactory completion. Also, I wish to express my thanks to Dr. P. K. Das of the Radiation Laboratory of the University of Notre Dame, for carrying out the laser flash and pulse radiolysis studies, reported in this thesis. I wish to acknowledge the help rendered by all members of the Chemistry faculty and in particular Professor P.S. Goel and Professor S. Chandrasekaran, during the course of my stay here.

I would like to make special mention of my laboratory colleagues, Dr. P. M. Scaria, Dr. C. V. Kumar, Dr. B. B. Lohray, Dr. B. A. R. C. Murty, Dr. R. K. Tikare, Mr. Mohd. Muneer, Mr. K. Ashok, Mr. S. Prathapan, Mr. K. R. Gopidas and Mr. D. Ramaiah, who have been of invaluable help to me throughout. I, sincerely, acknowledge the unreserved help rendered by Mr. B. L. Shyamal and Mr. N. Ahmad during my stay here.

Thanks are due to the Sophisticated Instruments Facility, Indian Institute of Science, Bangalore and the Regional Sophisticated Instrumentation Centre, CDRI, Lucknow for recording the ^{13}C NMR and mass spectra of some of the samples reported in this thesis.

Thanks are due to Mr. R. D. Singh for typing, Mr. R. K. Bajpai for the drawings, Mr. Bishambher Nath Shukla for cyclo-styling and Mr. Mumtaz Ahmad for the binding of this thesis.

Finally, I wish to express my deep appreciation and gratitude to my wife Sanjukta, for her patience, constant support and encouragement throughout my stay here.

R. Barik

CONTENTS

	Page
CERTIFICATE OF COURSE WORK ii
CERTIFICATE II iii
STATEMENT iv
ACKNOWLEDGEMENTS v
PREFACE viii
CHAPTER	
I. Phototransformations of 1-Aziridinyl- 1,2-dibenzoylalkenes 1
II. Phototransformations of 1-Imidazolyl- 1,2-dibenzoylalkenes 56
III. Phototransformations of 1-Triazolyl- 1,2-dibenzoylalkenes and Related Substrates 111
VITAE xi

PREFACE

The thesis entitled "Photochemical Investigations of Selected Organic Substrates Containing 1,2-Dibenzoylalkene Moieties and Related Systems" has been divided into three chapters.

Chapter I of the thesis deals with a brief survey of the photochemistry of simple 1,2-dibenzoylalkenes, followed by our studies on the steady-state and laser flash photolysis of aziridinyl-1,2-dibenzoylalkenes, 35a-d and 36a-d. The (E)-1-aziridinyl-1,2-dibenzoylethylenes 35a-d (Scheme I.5), upon steady-state photolysis, undergo facile ring-enlargement reactions, leading to pyrroline derivatives 37a-d, and also photofragmentation reactions, resulting in the formation of the cis- and trans-olefins 38a-d and 39a-d and a vinylnitrene intermediate, which subsequently rearranges to give the isoxazole 40. The (Z) 1-aziridinyl-1,2-dibenzoylethylenes 36a-d on the other hand undergo trans-cis photoisomerization leading to the corresponding E isomers 35a-d, which in turn, undergo further photoreactions leading to products such as 37-40. Laser flash photolysis studies of these substrates reveal transient absorption processes explainable in terms of singlet mediated cis-trans photoisomerization and also the formation of azomethine ylides.

Chapter II deals with the photochemical transformations of a few imidazolyl-1,2-dibenzoylalkenes 3a-e. Steady-state

photolysis of 1-imidazolyl-1,2-dibenzoylethylenes 3a-e (Schemes II.2 and II.3) reveals a variety of photoreactions depending on the nature of the substituents present in the imidazolyl moieties. These include electrocyclic ring-closure reactions leading to dihydrophenanthrenes 5a,b, phenanthrenes 6a,b, and dihydroisoquinoline derivatives 7a,c,d, intramolecular phenyl ring migration reactions giving rise to ketene derived acids 10d,e or esters 11d,e, and photofragmentation reactions leading to the trans-1,2-dibenzoylalkene 8 or 9 and imidazoles 1a-c. Laser flash photolysis of these substrates shows transient phenomena based on ketene formation and also photofragmentation reactions.

Chapter III deals with the steady-state and laser flash photolysis studies of a few 1-(1,2,3- and 1,2,4-triazolyl)-1,2-dibenzoylalkenes such as 3, 4, 8 and 9, and related substrates, 5 and 6 (Schemes III.2, III.3 and III.4). Product analysis reveals the involvement of several types of photoreactions depending on the nature of substituents present on the ethylenic moieties of these substrates. The (E)- and (Z)-1-benzotriazolyl-1,2-dibenzoylethylenes 3 and 4, upon steady-state irradiation, give rise to the 1,2-dibenzoylalkene-rearranged product 12a or 12b, the nitrogen-eliminated products 11 and 14, and also the bisbenzotriazolylbutane-1,2-dione derivatives 13 and 15, respectively. The benzotriazolylmaleate 5 and the benzotriazolylfumarate 6, on the other hand, undergo photochemical nitrogen loss, leading to biradical intermediates,

which either on subsequent rearrangement give rise to the indole-2,3-dicarboxylate 17, or reacts with the solvent to give the 2-phenylanilinofuramate 16. In contrast, the steady-state irradiation of the 1-(1H-1,2,4-triazolyl)-1,2-dibenzoylethylenes 8 and 9, leads to electrocyclic ring-closure products 19b and 19a, respectively, along with photofragmentation products 7 and 22a (or 22b). Laser flash photolysis studies, in several cases, reveal transient processes related to ketene and zwitterionic intermediates.

Note: The numbers of the various compounds given in the parentheses correspond to those given under the respective chapters.

CHAPTER I

PHOTOTRANSFORMATIONS OF 1-AZIRIDINYL- 1,2-DIBENZOYLALKENES

I.1 ABSTRACT

Photochemical transformations of a few aziridinyl substituted cis- and trans-1,2-dibenzoylethylenes have been examined to study the nature of the products formed in these cases and also the reaction pathways. Laser flash photolysis studies have been carried out to characterize the transients involved in these photochemical reactions. The substrates that we have examined in the present studies include several 1-aziridinyl-cis-1,2-dibenzoylethylenes such as (E)-1-(cis-2,3-diphenylaziridinyl)-1,2-dibenzoylethylene (35a), (E)-1-(trans-2,3-diphenylaziridinyl)-1,2-dibenzoylethylene (35b), (E)-1-(cis-2-benzyl-3-phenylaziridinyl)-1,2-dibenzoylethylene (35c), and (E)-1-(2-benzyl-cis-2,3-diphenylaziridinyl)-1,2-dibenzoylethylene (35d) and several 1-aziridinyl-trans-1,2-dibenzoylethylenes such as (Z)-1-(cis-2,3-diphenylaziridinyl)-1,2-dibenzoylethylene (36a),

(Z)-1-(trans-2,3-diphenylaziridinyl)-1,2-dibenzoylethylene (36b), (Z)-1-(cis-2-benzyl-3-phenylaziridinyl)-1,2-dibenzoylethylene (36c) and (Z)-1-(2-benzyl-cis-2,3-diphenylaziridinyl)-1,2-dibenzoylethylene (36d).

Irradiation of 35a in benzene, for example, gave a mixture of 2,3-dibenzoyl-cis-4,5-diphenyl- Δ^2 -pyrroline (37a, 45%), 3-benzoyl-5-phenylisoxazole (40, 4%), cis-stilbene (38a, 15%) and trans-stilbene (39a, 17%), in addition to a small amount of unidentified polymeric material. Similar results were obtained in the irradiations of 35b, 35c and 35d.

Irradiation of the Z isomers 36a-d in benzene, on the other hand, gave mainly the corresponding E isomers 35a-d, along with small amounts of the photoproducts derived from these E isomers.

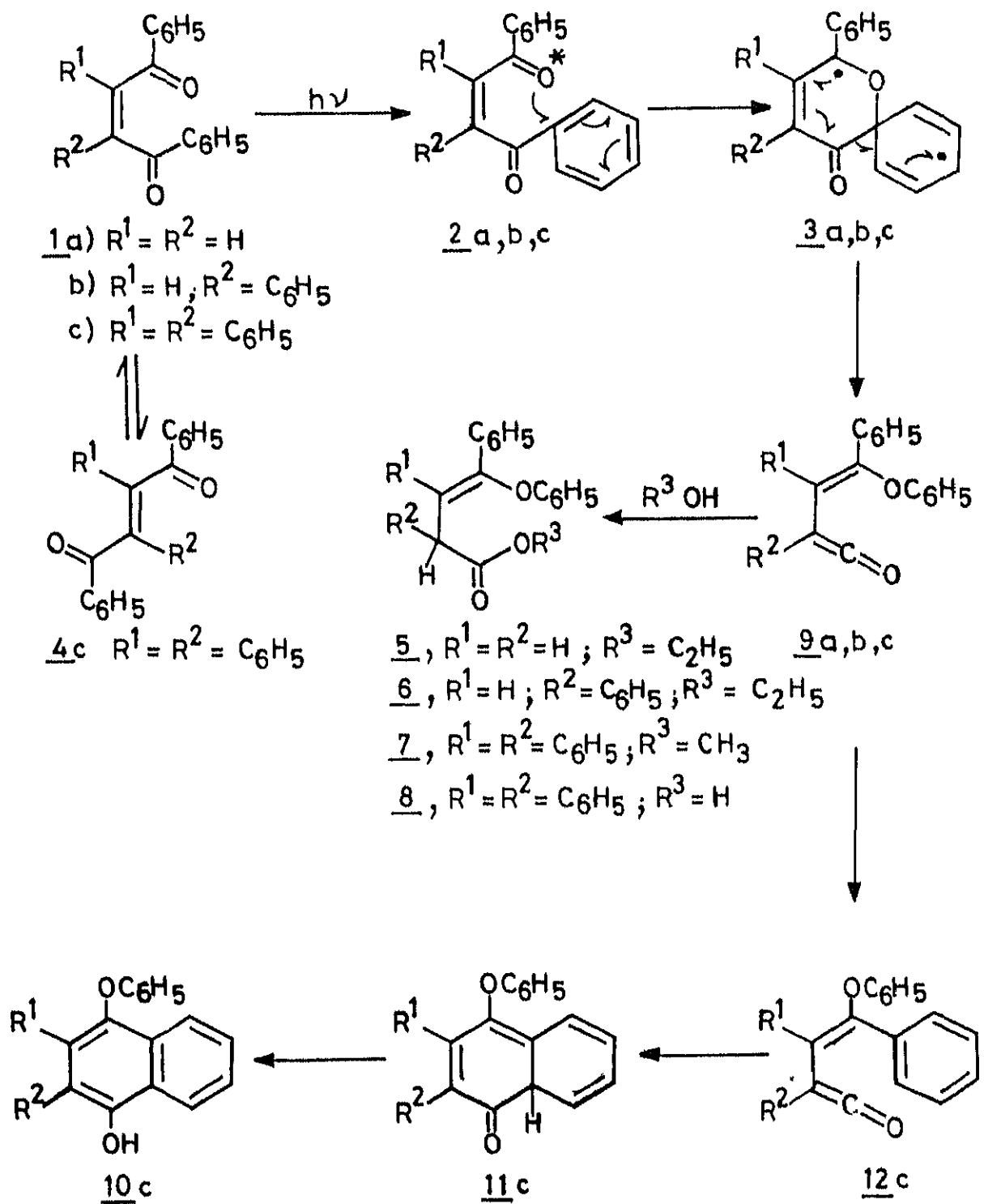
Products isolated from steady-state photolysis suggested facile ring-expansion, yielding pyrrolines as well as extrusion of alkenes from aziridines, giving rise to nitrene fragments, which undergo subsequent ring-closure to give isoxazole. Laser flash photolysis studies showed transient absorption changes explainable in terms of cis-trans photoisomerization and formation of azomethine ylides. The latter are also observed upon steady-state irradiation of these aziridinyl-1,2-dibenzoylethylenes in EPA glass at 77 K.

I.2 INTRODUCTION

Past investigations by Griffin and O'Connell¹ and also by Zimmerman et al.^{2,3} have shown that 1,2-dibenzoylalkenes (1a-c) undergo interesting photorearrangements giving rise to ketene derived products (Scheme I.1). Thus, it has been observed that the photolysis of cis-1,2-dibenzoylethylene (1a) in methanol, for example, gives ethyl 4-phenoxy-4-phenyl-3-butenate (5). Similarly, dibenzoylstyrene (1b) and dibenzoylstilbene (1c) give analogous products, 6 and 7, respectively. Padwa et al.⁴ have observed that trans-dibenzoylstilbene (1c), upon irradiation, undergoes cis-trans photoisomerization, followed by subsequent rearrangement to give a ketene intermediate (9c), which on further rearrangement leads to 1-hydroxy-2,3-diphenyl-4-phenoxy-naphthalene (10c) or reacts with solvents to give 2,3,4-triphenyl-4-phenoxy-3-butenic acid (8) or the corresponding ester (7). Sugama and Kashima,⁵ on the other hand, have shown that the photolysis of 1,2-dibenzoylethylene (1a) in acidic methanol gives a mixture of 1,2-dibenzoylmethoxyethane, methyl 4-phenoxy-4-phenyl-3-butenate and 2,3-diphenylfuran.

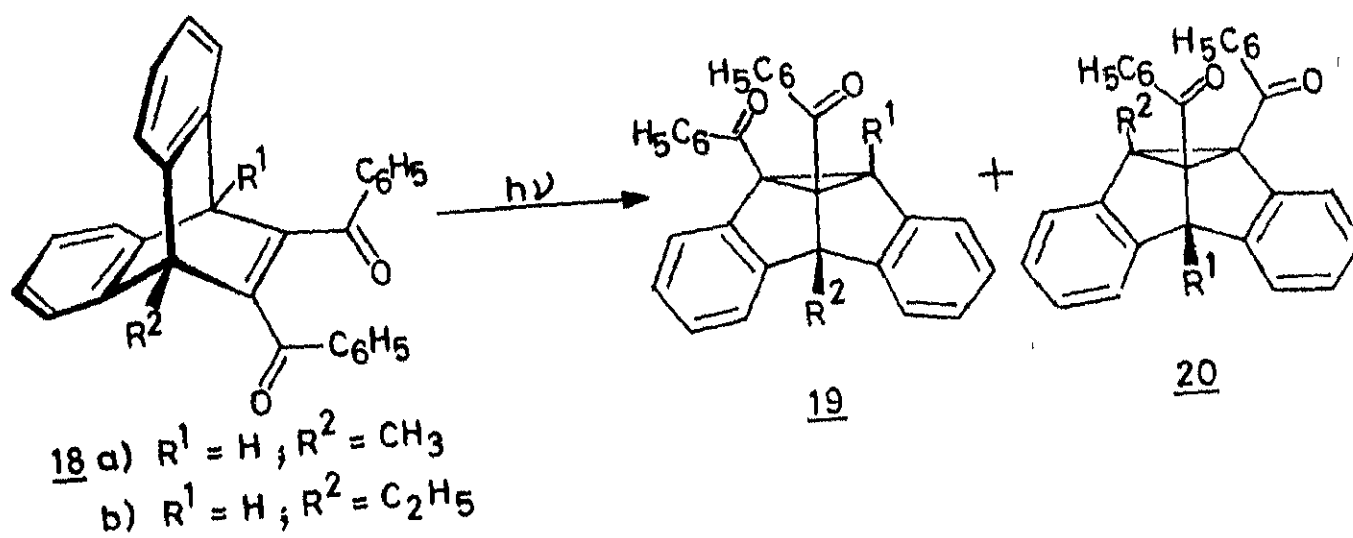
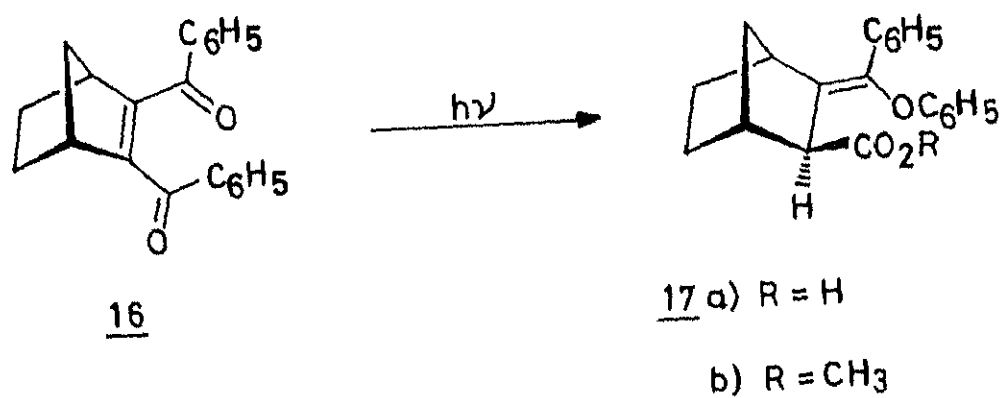
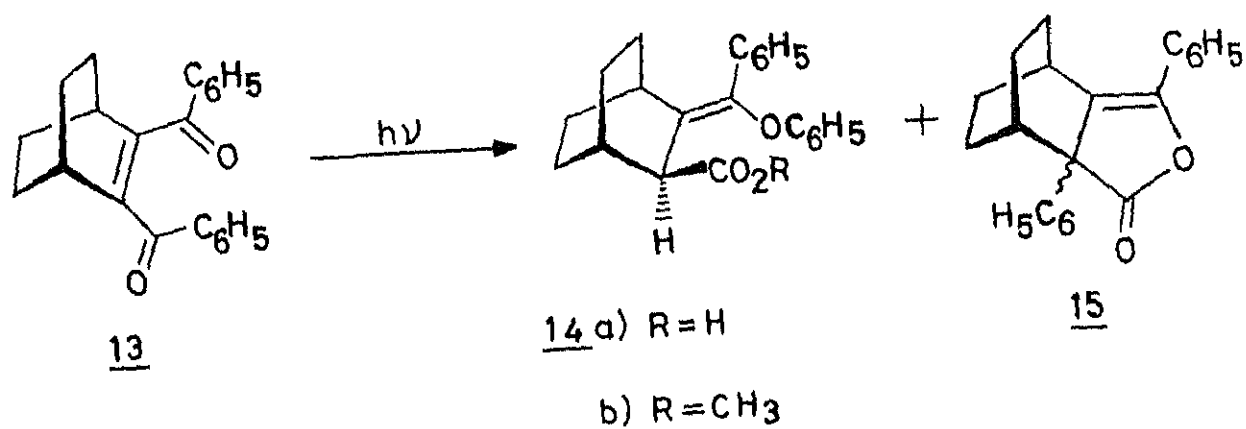
Recent studies⁶⁻⁸ have shown that substrates containing 1,2-dibenzoylalkene moieties undergo the photorearrangement exclusively, if the cis-trans isomerization possibility is prevented through geometric constraints. Thus, it has been observed that the photolysis of 2,3-dibenzoylbicyclo[2.2.2]-oct-2-ene (13) in benzene, for example, gives a mixture of

Scheme 1.1



3-(phenoxyphenylmethylene)bicyclo[2.2.2]octane-2-carboxylic acid (14a) and the lactone (15)⁶ (Scheme I.2), whereas the irradiation of 2,3-dibenzoylbicyclo[2.2.2]hept-2-ene (16) in benzene gives exclusively the corresponding carboxylic acid (17a).^{7,8} As part of our continuing interest in the photorearrangements of 1,2-dibenzoylalkenes, the phototransformations of several substrates containing 1,2-dibenzoylalkene moieties such as 1,4- and 1,2-epoxy compounds,^{9,10} dibenzobarrelenes,^{10,11} and 1-pyrazolyl-1,2-dibenzoylalkenes^{12,13} have been investigated. In general, it has been observed that the photorearrangements of substituted 1,2-dibenzoylalkenes depend strongly on the nature of the substituents. Thus, it has been observed that dibenzobarrelenes containing 1,2-dibenzoylalkenes^{10,11} undergo the di- π -methane rearrangement (Zimmerman rearrangement¹⁴), giving rise to dibenzoyl substituted dibenzosemibulvalenes (19a,b and 20a,b, Scheme I.2). In contrast, 1-pyrazolyl-1,2-dibenzoylalkenes^{12,13} undergo the 1,2-dibenzoylalkene rearrangement¹⁻³ and also electrocyclic reactions involving aryl substituents present in the pyrazolyl ring.

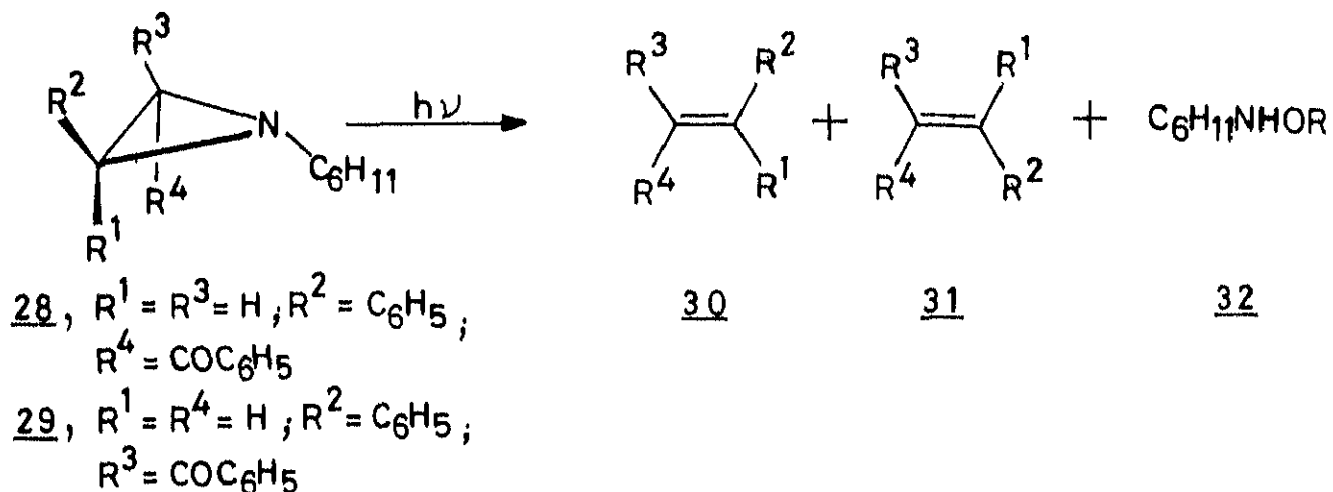
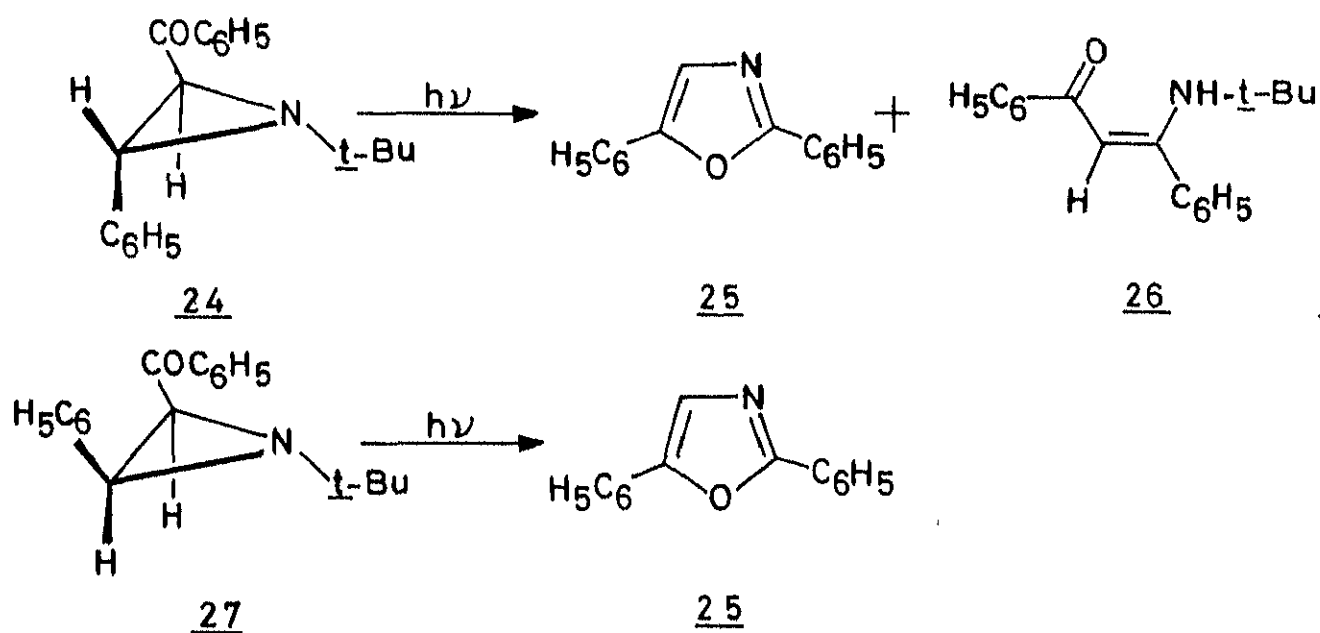
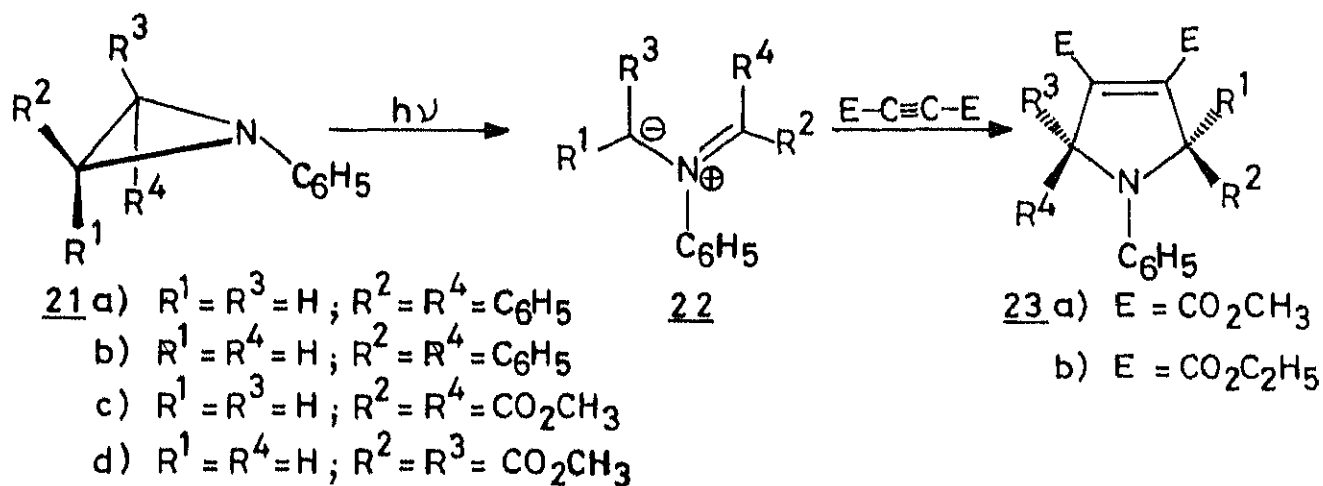
In the present studies, we have examined the steady-state phototransformations of a few selected 1-aziridinyl-1,2-dibenzoylalkenes to investigate the nature of the products formed and also the reaction pathways followed in these cases. Flash photolysis studies have also been carried out to characterize the transients involved in these reactions. The photoreactions

Scheme 1.2

of 1-aziridinyl-1,2-dibenzoylalkenes can, in principle, proceed through two different pathways - one involving the reaction of the aziridine component and the other related to the dibenzoylalkene fragment. It may be pointed out in this connection that the phototransformations of several aziridine derivatives have been reported in the literature.¹⁵⁻¹⁷ Aziridines, in general, undergo electrocyclic ring opening reactions involving carbon-carbon bond cleavage to give azomethine ylides.^{18,19} It has also been observed that several 2-benzoylaziridines undergo photochemical C-N and C-C bond cleavage leading to olefins and other ring enlarged products²⁰⁻²² (Scheme I.3).

The substrates that we have examined in the present studies include several 1-aziridinyl-cis-1,2-dibenzoylalkenes and 1-aziridinyl-trans-1,2-dibenzoylalkenes such as (E)-1-(cis-2,3-diphenylaziridinyl)-1,2-dibenzoylethylene (35a), (E)-1-(trans-2,3-diphenylaziridinyl)-1,2-dibenzoylethylene (35b), (E)-1-(cis-2-benzyl-3-phenylaziridinyl)-1,2-dibenzoylethylene (35c), (E)-1-(2-benzyl-cis-2,3-diphenylaziridinyl)-1,2-dibenzoylethylene (35d), (Z)-1-(cis-2,3-diphenylaziridinyl)-1,2-dibenzoylethylene (36a), (Z)-1-(trans-2,3-diphenylaziridinyl)-1,2-dibenzoylethylene (36b), (Z)-1-(cis-2-benzyl-3-phenylaziridinyl)-1,2-dibenzoylethylene (36c) and (Z)-1-(2-benzyl-cis-2,3-diphenylaziridinyl)-1,2-dibenzoylethylene (36d).

Scheme I.3

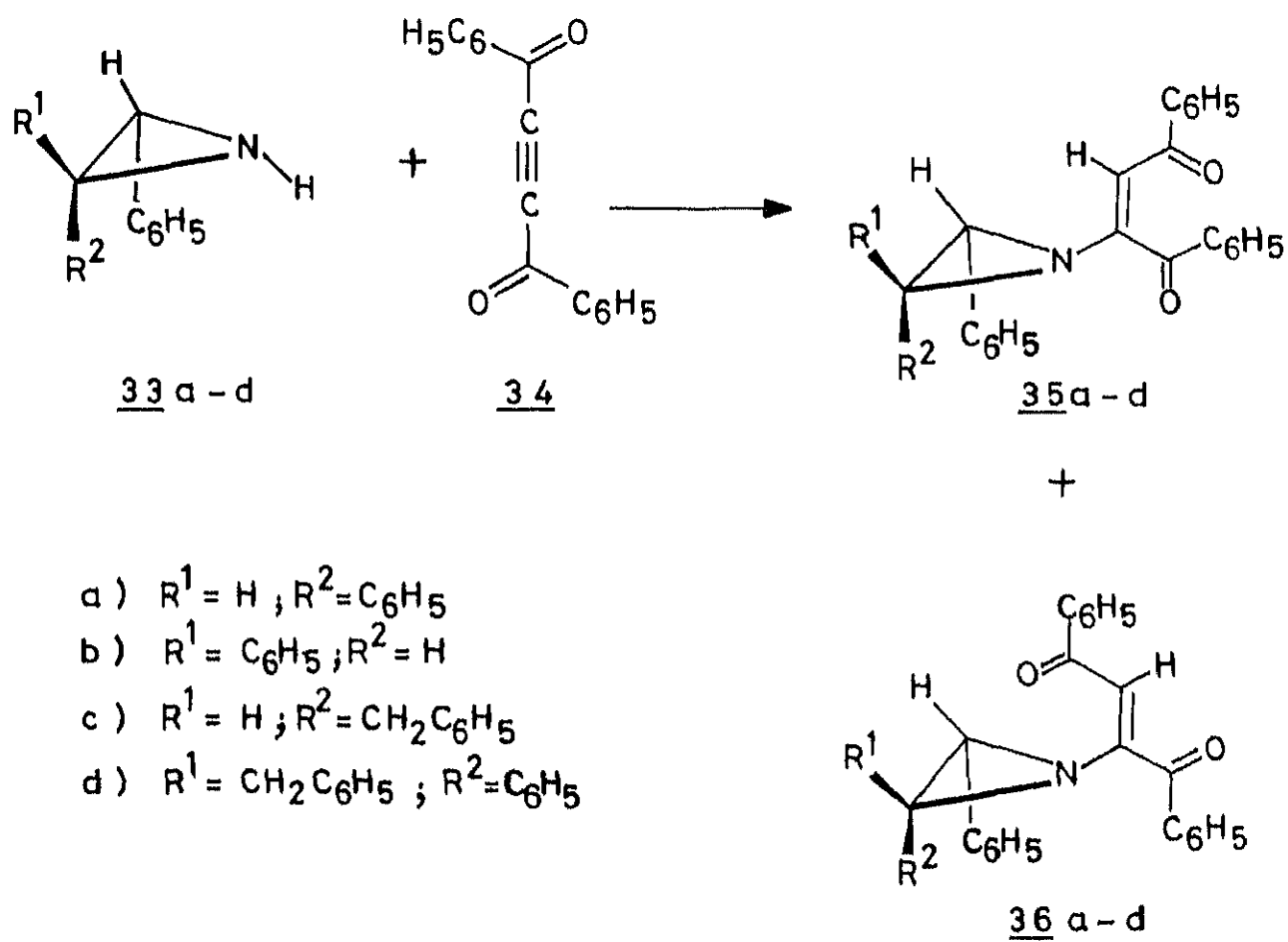


I.3 RESULTS AND DISCUSSION

I.3.1 Preparation of Starting Materials. Nucleophiles such as amines, hydrazines, heterocyclic bases etc. are known to add to acetylenic substrates to give the corresponding 1:1 adducts.²⁴⁻²⁷ We have prepared the (E)-1-aziridinyl-1,2-dibenzoylethylenes (35a-d) and the (Z)-1-aziridinyl-1,2-dibenzoylethylenes (36a-d) in yields ranging between 35-60% and 30-50%, respectively through the addition reaction of the appropriate aziridines (33a-d) with dibenzoylacetylene (DBA, 34) (Scheme I.4). The structures of 35a-d and 36a-d have been established on the basis of analytical results and spectral evidence. The geometry across the carbon-carbon double bond in all these adducts has been ascertained on the basis of their ¹H NMR and electronic spectra. It has been observed that the vinyl protons in the E isomers (35a-d) appear in the range δ 5.7-6.3, whereas in the Z isomers (36a-d), they are downfield shifted and appear in the range δ 6.32-6.75. Similar chemical shift differences of vinyl protons have been observed in the case of aminomaleates and fumarates, formed through the reaction of secondary amines with dimethyl acetylenedicarboxylate (DMAD).^{24a}

Further, it has been observed that amine-substituted 1,2-dibenzoylalkenes having E configuration show characteristic long-wavelength absorption maxima around 345 nm, whereas the corresponding absorption maxima for the respective Z isomers appear around 390 nm.^{24b} The 1-aziridinyl-1,2-dibenzoylethylenes 35a-d

Scheme 1.4

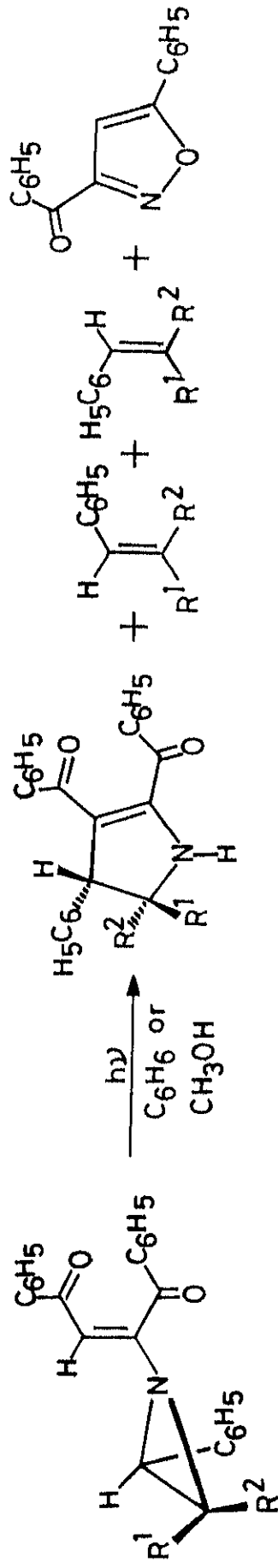


showed absorption maxima around 312-318 nm and hence have been assigned as the E isomers, whereas the Z adducts 36a-d showed the corresponding absorption maxima around 320-330 nm.

I.3.2 Preparative Photochemistry and Product Identification. Irradiation of 35a in benzene gave a mixture of 2,3-dibenzoyl-cis-4,5-diphenyl- Δ^2 -pyrroline (37a, 45%), 3-benzoyl-5-phenylisoxazole (40, 4%), cis-stilbene (38a, 15%) and trans-stilbene (39a, 17%), in addition to a small amount (15%) of unidentified polymeric material (Scheme I.5). Similarly, the irradiation of 35b in benzene gave a mixture of 2,3-dibenzoyl-trans-4,5-diphenyl- Δ^2 -pyrroline (37b, 44%), 40 (5%), 38a (15%) and 39a (18%), besides some polymeric material (17%). Similar results were obtained when the irradiations of 35a and 35b were carried out in methanol.

The structures of 37a and 37b have been arrived at on the basis of analytical results, spectral data and chemical evidence. The ^1H NMR spectrum of 37a, for example, showed two doublets at δ 3.15 ($J_{4,5} = 7.5$ Hz, 1 H) and δ 4.38 ($J_{4,5} = 7.5$ Hz, 1 H), assigned to C-4H and C-5H protons, respectively. The coupling constants of 7.5 Hz would support the syn orientation of these two protons. The NH protons of 37a appeared as a broad singlet at δ 6.85 (1 H, D_2O -exchangeable), whereas the aromatic protons appeared as a complex multiplet centered at δ 7.65 (20 H). The ^1H NMR spectrum of 37b, likewise, showed doublets at δ 3.30 ($J_{4,5} = 13$ Hz, 1 H, C-4H) and δ 4.60 ($J_{4,5} = 13$ Hz, 1 H, C-5H),

Scheme 1.5



35a-d

38

39

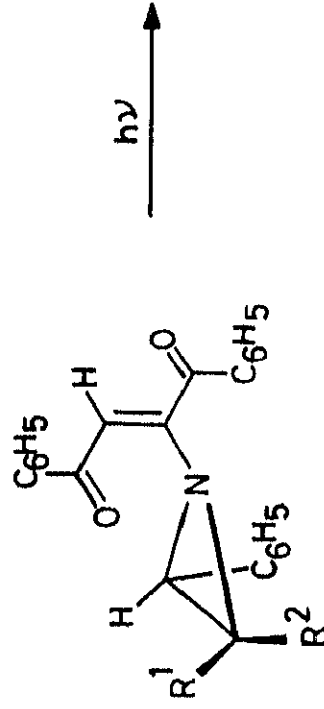
40

(8 - 45%)

(15 - 35%)

(17 - 30%)

(3 - 13%)



36a-d

36a-d

40

39

a) $R^1 = H$; $R^2 = C_6H_5$

b) $R^1 = C_6H_5$; $R^2 = H$

c) $R^1 = H$; $R^2 = CH_2C_6H_5$

d) $R^1 = CH_2C_6H_5$; $R^2 = C_6H_5$

(0 - 3%)

(6 - 16%)

(4 - 18%)

(7 - 17%)

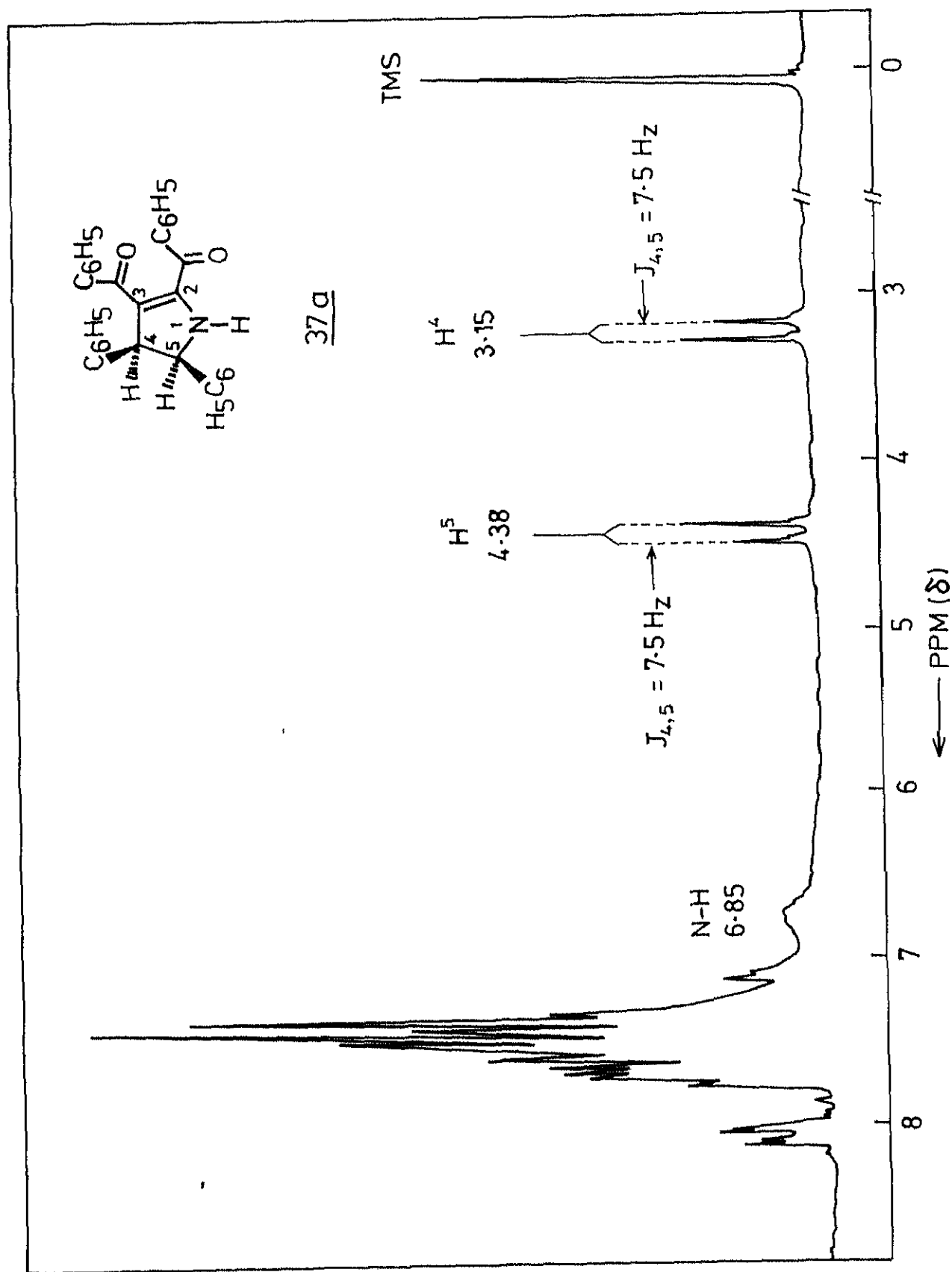


Figure I.1 ^1H NMR spectrum (90 MHz) of **37a**

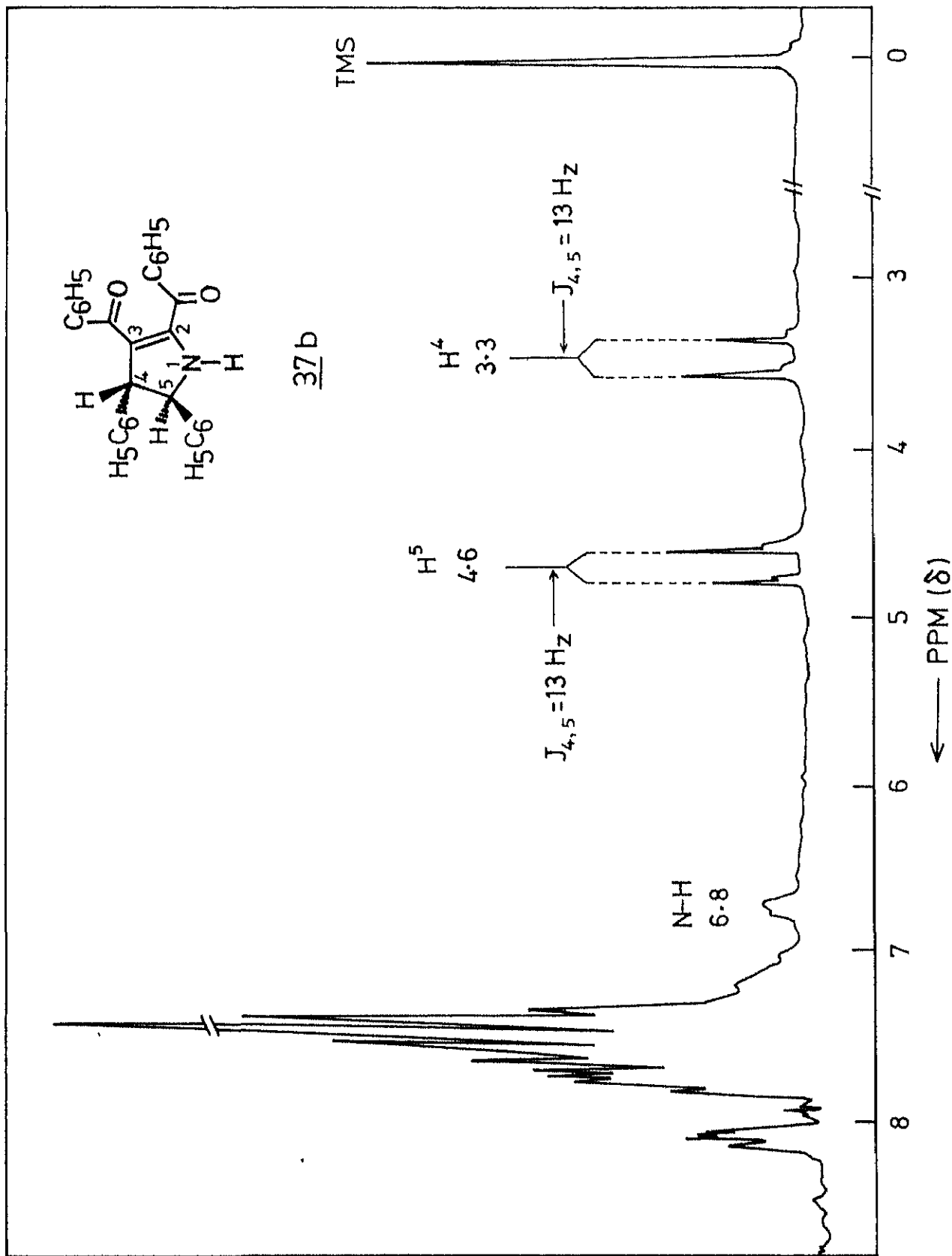
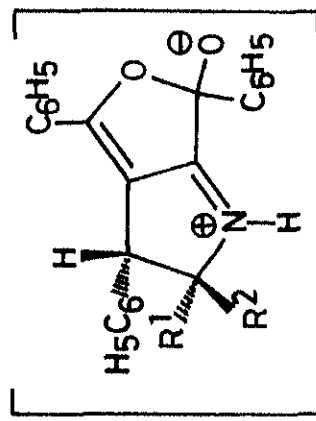
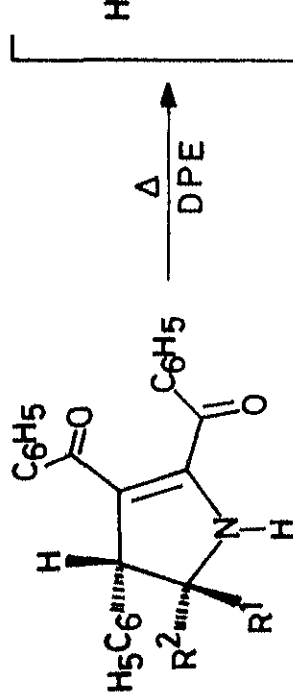


Figure I-2 ¹H NMR spectrum (90 MHz) of **37b**.

respectively. The coupling constant of 13 Hz, however, indicates that both C-4H and C-5H protons are anti with respect to each other. The NH and aromatic protons appeared at δ 6.8 (broad singlet, 1 H, D₂O-exchangeable) and δ 7.1-8.2 (m, 20 H), respectively (see Figures I.1 and I.2).

Further confirmation of the structures of 37a and 37b was derived from chemical evidence. Air-oxidation of 37a and 37b gave, in each case, 2,3-dibenzoyl-4,5-diphenylpyrrole (43), in nearly quantitative yield. Heating of 37a in diphenyl ether ($\sim 255^\circ\text{C}$), on the other hand, gave a mixture of 3-benzoyl-2,4,5-triphenylpyrrole (44, 26%) and 43 (54%). Similarly, 37b on heating in diphenyl ether under analogous conditions gave a mixture of 43 (51%) and 44 (30%). The structures of both 43 and 44 were confirmed through their syntheses from 4,5-diphenylpyrrole-2,3-dicarboxylic acid (46)²⁸ and 2,4,5-triphenylpyrrole-3-carboxylic acid (47),²⁹ respectively. The formation of 43 and 44 from 37a and 37b can be understood in terms of the pathway shown in Scheme I.6.

Irradiation of 35c in benzene gave a mixture of 5-benzyl-2,3-dibenzoyl-4-phenyl- Δ^2 -pyrroline (37c, 45%), 40 (5%), cis- β -benzylstyrene (38c, 15%) and trans- β -benzylstyrene (39c, 17%). Similar results were also obtained when 35c was irradiated in methanol. The ¹H NMR spectrum of 37c showed a doublet at δ 3.25 ($J_{4,5} = 5$ Hz, 1 H) as the X part of an A₂BX system, assigned to C-4H proton, a multiplet at δ 2.9 (1 H) as the B part of the

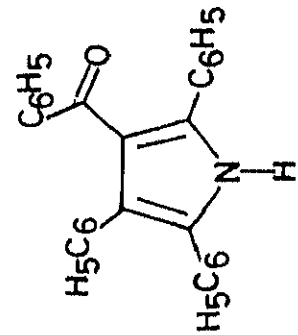
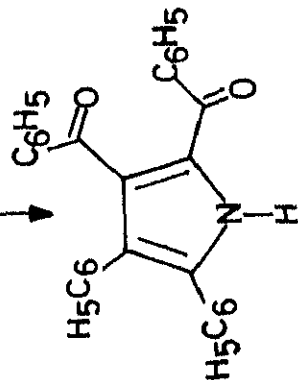


37 a, b

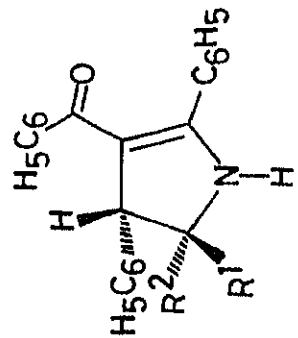
- a) $R^1 = H; R^2 = C_6H_5$
 b) $R^1 = C_6H_5; R^2 = H$

42 a, b

$-\text{CO}$



$[\text{O}_2]$



43

44

45



46

47

48

49

50

51

52

53

54

55

56

57

58

59

60

61

62

63

64

65

66

67

68

69

70

71

72

73

74

75

76

77

78

79

80

81

82

83

84

85

86

87

88

89

90

91

92

93

94

95

96

97

98

99

100

101

102

103

104

105

106

107

108

109

110

111

112

113

114

115

116

117

118

119

120

121

122

123

124

125

126

127

128

129

130

131

132

133

134

135

136

137

138

139

140

141

142

143

144

145

146

147

148

149

150

151

152

153

154

155

156

157

158

159

160

161

162

163

164

165

166

167

168

169

170

171

172

173

174

175

176

177

178

179

180

181

182

183

184

185

186

187

188

189

190

191

192

193

194

195

196

197

198

199

200

201

202

203

204

205

206

207

208

209

210

211

212

213

214

215

216

217

218

219

220

221

222

223

224

225

226

227

228

229

230

231

232

233

234

235

236

237

238

239

240

241

242

243

244

245

246

247

248

249

250

251

252

253

254

255

256

257

258

259

260

261

262

263

264

265

266

267

268

269

270

271

272

273

274

275

276

277

278

279

280

281

282

283

284

285

286

287

288

289

290

291

292

293

294

295

296

297

298

299

300

301

302

303

304

305

A₂BX system, assigned to the C-5H proton and another multiplet at δ 2.7 (2 H) as the A₂ part of the same A₂BX system, assigned to the CH₂ protons.³⁰ The NH and the aromatic protons appeared at δ 5.15 (broad singlet, 1 H, D₂O-exchangeable) and δ 6.8-7.9 (m, 20 H), respectively.

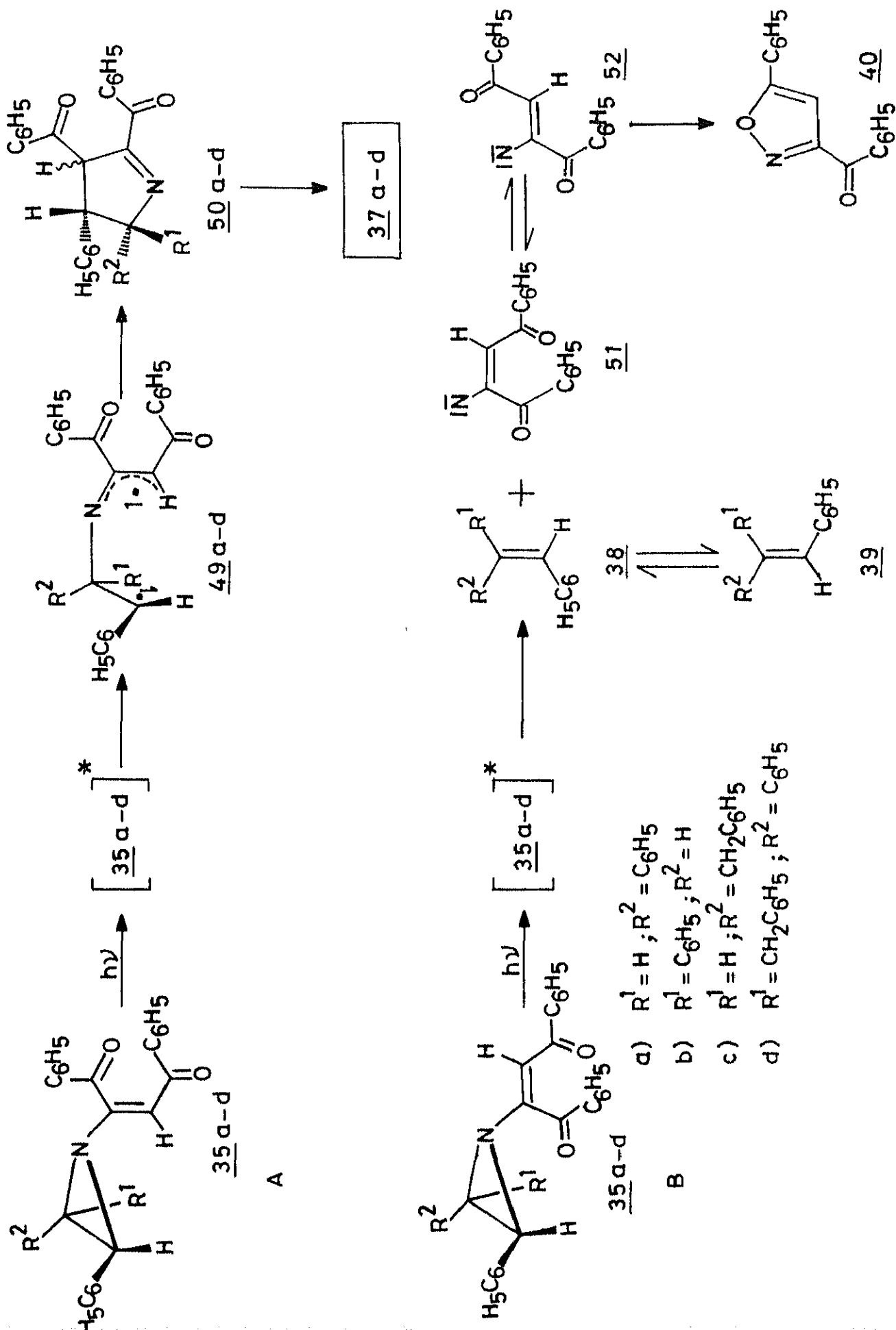
Photolysis of 35d in benzene, on the other hand, gave a mixture of 5-benzyl-2,3-dibenzoyl-cis-4,5-diphenyl- Δ^2 -pyrroline (37d, 10%), 40 (11%), cis- β -benzylstilbene (38d, 35%) and trans- β -benzylstilbene (39d, 30%). Similar results were obtained when the photolysis of 35d was carried out in methanol. The ¹H NMR spectrum of 37d showed a singlet at δ 3.45 (1 H), assigned to the C-4H proton (compared to the assignments in 37a and 37b) and a quartet at δ 2.8 (2 H), assigned to the methylene protons. The NH proton appeared as a broad singlet at δ 6.8 (1 H, D₂O-exchangeable), whereas the aromatic protons appeared as a complex multiplet at δ 7.1-8.1 (25 H).

Irradiation of the Z isomers 36a-d in benzene, on the other hand, gave mainly the corresponding E isomers (35a-d), along with small amounts of the photoproducts derived from these E isomers. Thus, the irradiation of 36a, for example, in benzene for 2 h gave a 30% yield of the E isomer 35a, along with a mixture of 37a (11%), 38a (8%), 39a (10%) and unchanged starting material (36a, 22%). In addition, a small amount (15%) of an unidentified polymeric material could also be isolated from this run. Similar results were obtained in the photolysis of 36b, 36c and 36d.

I.3.3 Discussion. Examination of the products from the photoreactions of the (E)-aziridiny1-1,2-dibenzoylethylenes 35a-d reveals that two important pathways are followed in these cases. One of these involves a ring enlargement of the vinylaziridine moiety to give the pyrroline derivatives 37a-d, whereas the other involves a photofragmentation, giving rise to the deaminated olefins 38a-d and 39a-d and the vinylnitrene fragment 51, which ultimately leads to the isoxazole 40 (Scheme I.7).

Vinylaziridine Rearrangement. Although several examples of the photochemical ring enlargement of vinylcyclopropanes to give cyclopentene derivatives are reported in the literature,^{31,32} the analogous vinylaziridine rearrangement has not been studied in detail. A reasonable explanation for the formation of the pyrroline derivatives 37a-d in the photoreactions of 35a-d, would involve a vinylaziridine rearrangement of the appropriate ground state conformers. It is to be noted that the pyrrolines 37a-d are formed in yields ranging between 8-45% and that these reactions proceed in both stereospecific and regioselective manner. Thus, we find that 35a containing two cis-phenyl groups in the aziridine ring gives rise to, exclusively, the cis-4,5-diphenylpyrroline 37a, whereas 35b, containing two trans-phenyl substituents gives rise to the trans-4,5-diphenylpyrroline 37b. In the case of unsymmetrically substituted aziridines 35c and 35d, however, the corresponding pyrrolines 37c and 37d are formed through stereospecific and regioselective pathways.

Scheme I.7



Although the conformational preferences of 1-aziridinyl-1,2-dibenzoylalkenes 35a-d are not known, it is reasonable to assume, on the basis of the conclusions reached for vinylcyclopropane³³ and some of its methyl derivatives³⁴ and also for several aziridinyl ketones,³⁵ that the conformational minima in these systems will correspond to the s-trans and nonsymmetrical s-cis or gauche conformation with a dihedral angle between 70° and 80°. It is to be noted that only the s-cis or gauche conformer can lead to the pyrroline derivatives (37a-d). Whether the photochemical ring-enlargement reactions of 35a-d, involving C-N bond cleavage proceed in a symmetry allowed concerted manner or through singlet diradical intermediates such as 49a-d, shown in Scheme I.7, is not very clear. Mention may be made in this connection that several examples of photochemical C-N bond cleavage have been observed in different aziridinyl ketones.^{35,36} The ring-enlargement reactions of 35a-d appear to be analogous to the photorearrangements of vinylcyclopropanecarboxylates, which have been studied earlier by Jorgenson and Heathcock.³²

Photochemical Fragmentation Reaction. It is quite likely that the symmetrically bisected s-trans conformer B (Scheme I.7) is the precursor of the fragmentation products from 35a-d. In the excited state, both the C-N bonds of these aziridinyl-1,2-dibenzoylalkenes will be considerably weakened due to the overlap of these bond orbitals with the π -systems and consequently, the loss of the vinylnitrene moiety 51, leading to the alkenes 38a-d

and 39a-d, would be predictable. This vinylnitrene intermediate can subsequently be transformed to the isoxazole 40, through the appropriate isomer 52 (Scheme I.7). Such photochemical loss of the nitrene fragments from the corresponding aziridinyl-1,2-dibenzoylalkenes 35a-d is analogous to the loss of carbene fragments from cyclopropyl olefinic esters.³² It may be mentioned in this connection that vinylnitrene intermediates, formed on thermolysis of vinylazides, are known to undergo intramolecular cyclization with carbonyl functionalities to give isoxazole derivatives.³⁷

I.3.4 Laser Flash Photolysis Studies.³⁸

As shown in Figure I.3, the absorption spectrum of each of the aziridinyl-dibenzoylalkenes under study is characterized by low-lying, moderately intense band system at 300-420 nm ($\epsilon_{\text{max}} = (10-20) \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$). Between the cis and the trans isomers, the absorption maxima of the latter are red-shifted by 8-14 nm. Although the ϵ_{max} values are lower for the trans isomers, they show enhanced absorption at longer wavelengths (340-420 nm). Because of relatively high extinction coefficients ($(5-10) \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$) at 337.1 nm, solutions containing the dibenzoylalkenes at submillimolar concentrations could be conveniently flash-photolyzed using nitrogen laser pulse at this wavelength. In the following sections we are presenting the results concerning the transient phenomena observed upon laser flash photolysis of the aziridinyl-dibenzoylalkenes in benzene and plausible assignments and interpretations.

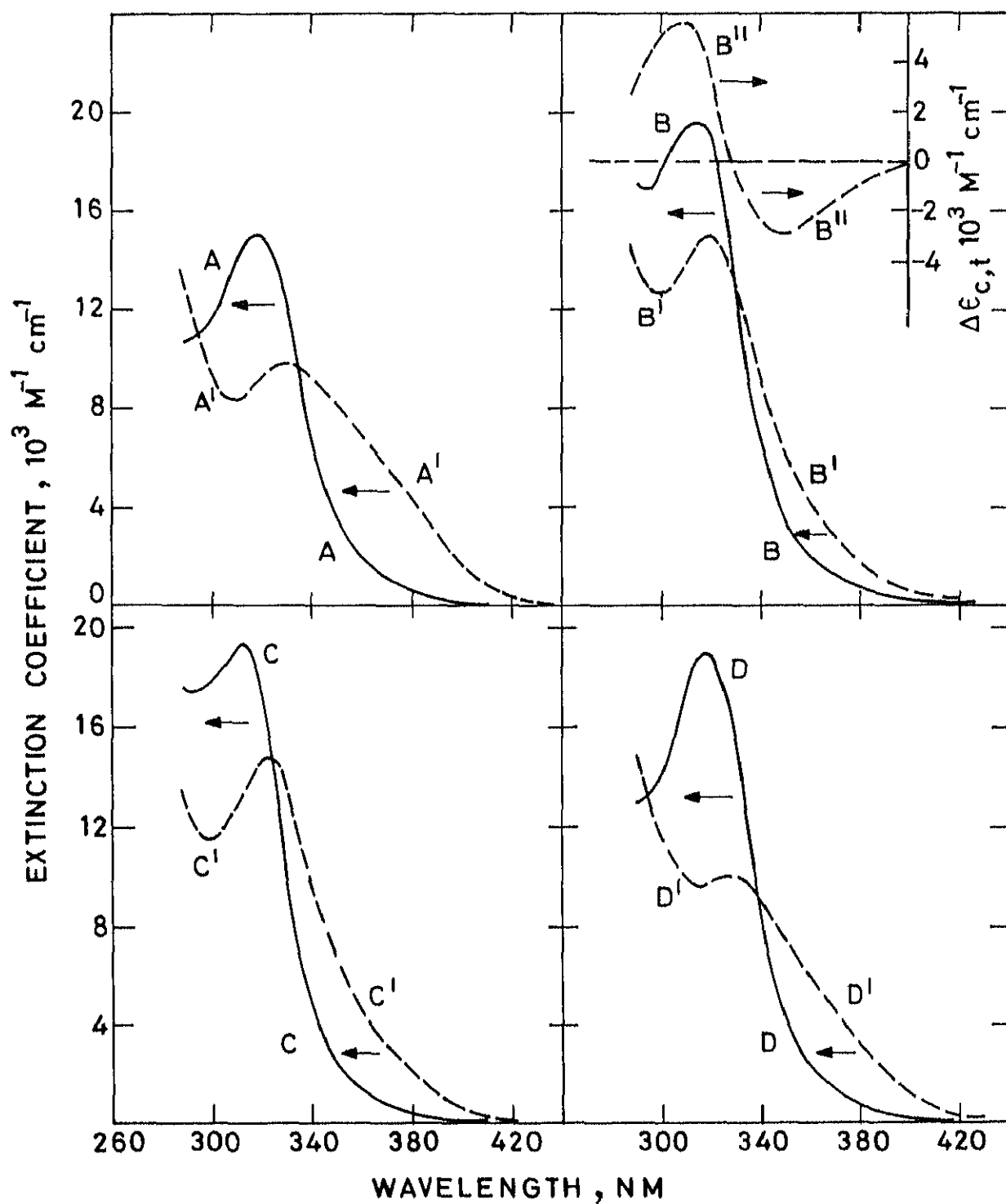


Figure 1.3 Absorption spectra of 1-aziridinyl(-1,2-dibenzoyl)-alkenes in benzene: A, 35a, B, 35b, C, 35c; D, 35d, A', 36a; B', 36b, C', 36c, D', 36d. The curve B'' is the difference absorption spectrum (trans→cis) for 35b and 36b

(E)-1-Aziridinyl-1,2-dibenzoylalkenes, 35a-d. Upon

337.1 nm laser flash photolysis, substrates 35a-d show very similar transient processes. Using 35b as example, these are illustrated in Figure 1.4. In terms of absorption spectral changes, the following have been noted. First, a pronounced ground-state bleaching (negative absorbance change) occurs at 300 - 335 nm; this does not show any sign of recovery over the longest time-scale ($\sim 100 \mu\text{s}$) available to us. Second, a long-lived (or 'permanent') photoproduct showing positive absorbance change at 335-400 nm ($\lambda_{\text{max}} = 345\text{-}350 \text{ nm}$) is formed. Third, a minor transient absorbing at 550-700 nm undergoes slow decay ($\tau > 10 \mu\text{s}$). Fourth, the slow growth of a minor product is observed at 420-440 nm (concomitant with the decay of the 550-700 nm species). The third and fourth transient phenomena have not been observed to any significant extent in the case of 35c and 35d.

Detailed studies using oxygen, di-tert-butylnitroxide (DTBN), and ferrocene show that these typical triplet quenchers have no effect on the yields and kinetics of the transients or photoproducts discussed above. Thus, the involvement of a long-lived triplet either as one of the transient species seen in laser flash photolysis or as a precursor of the photoproduct(s) is ruled out. The most plausible explanation for the absorption spectral changes at 300-400 nm may be sought in terms of cis-trans isomerization and/or ring-enlargement products 50a-d or fast

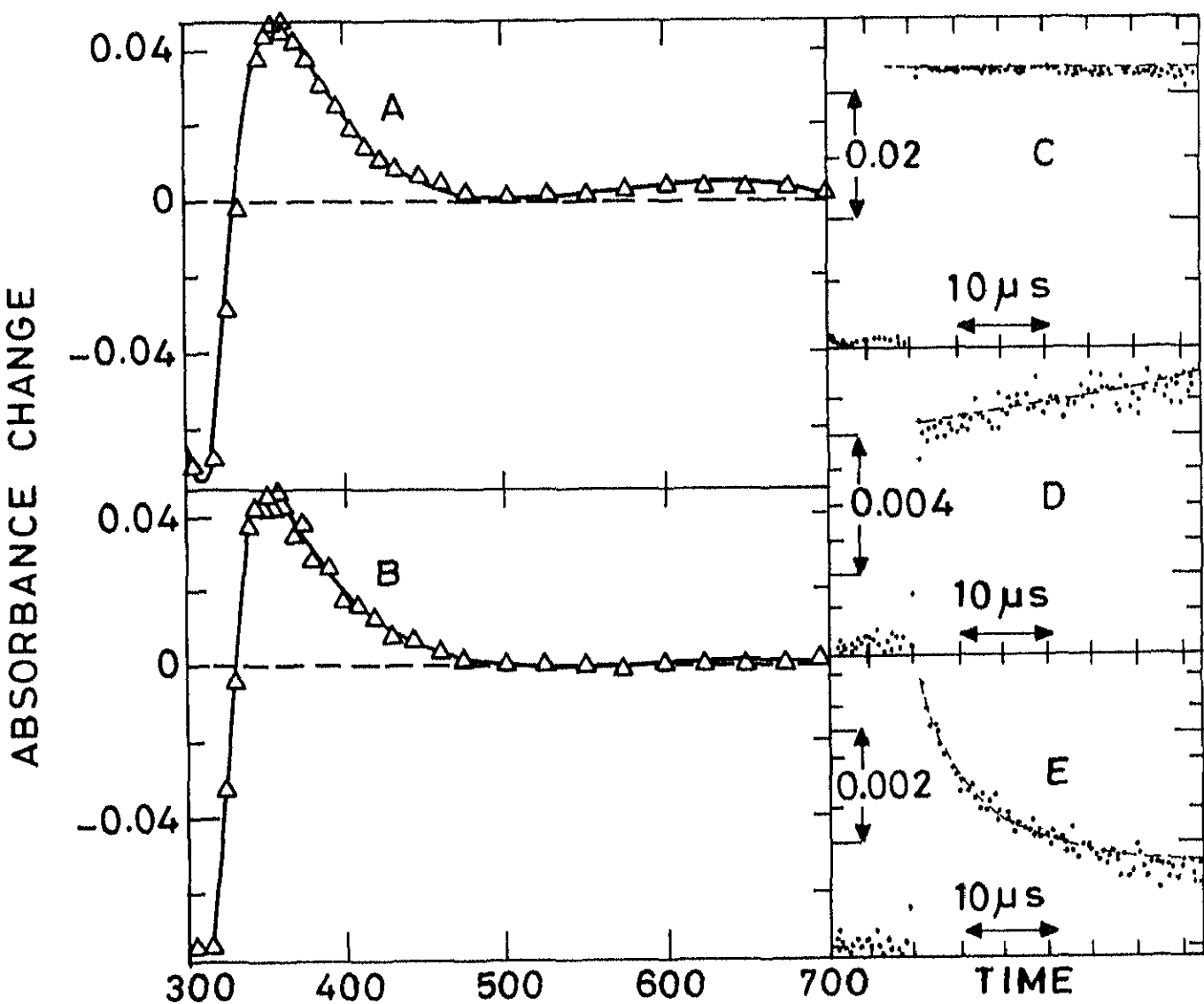
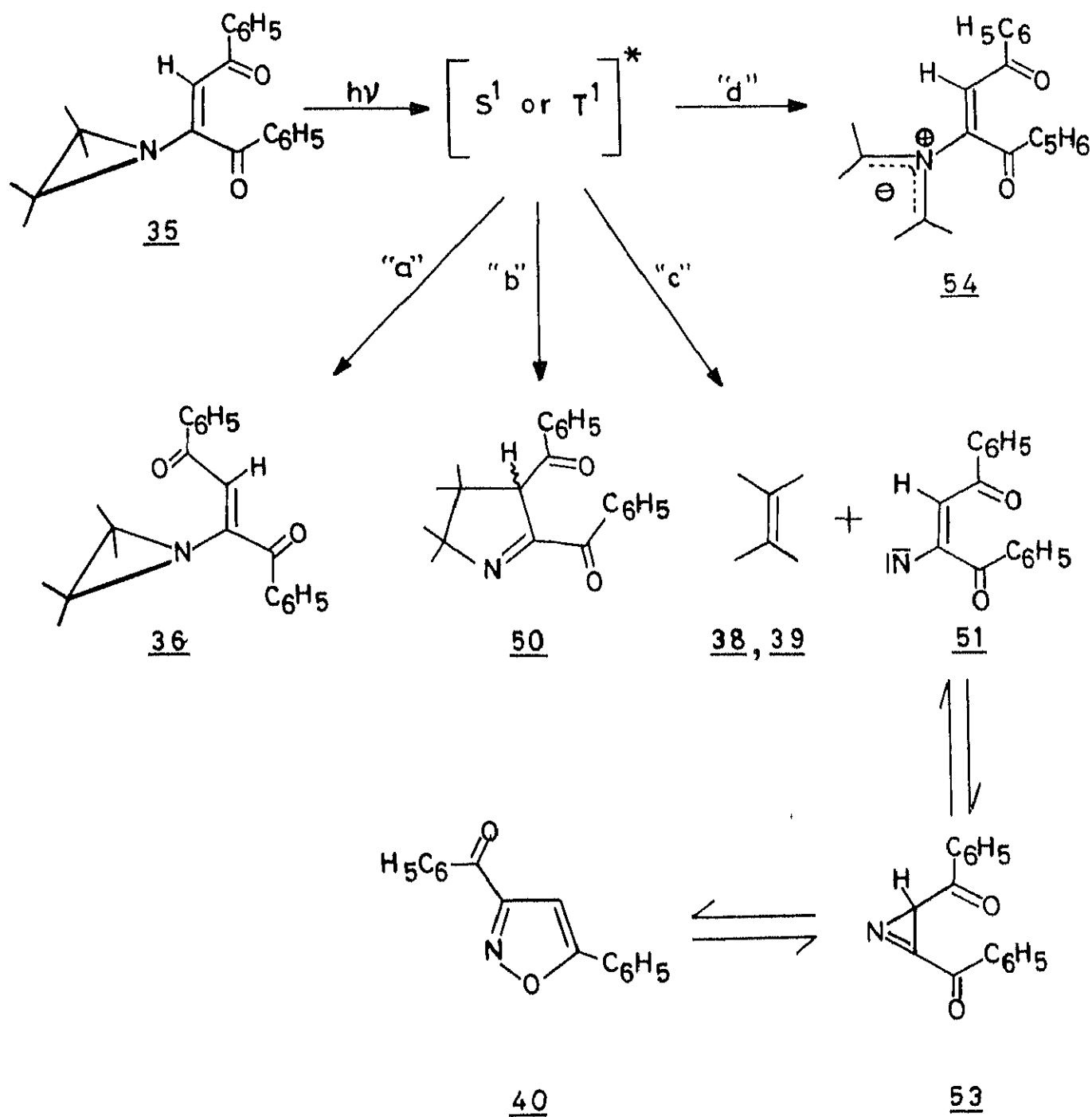


Figure 1.4 Transient absorption spectra observed upon 337.1 nm laser flash photolysis of 35b in benzene at 2 μs (A) and 30 μs (B), following the laser flash. Representative kinetic traces at 355 (C) 440 (D) and 600 nm (E) are also shown.

formation of a long-lived species, namely, the nitrene 51 (or nitrene-derived products). These phototransformations are shown in pathways 'a-c' in Scheme I.8. Because of reduced conjugation in the ring-enlargement product 50 (relative to the parent dibenzoylalkene), this appears to be the least likely candidate to account for the red-shifted absorption changes evident at 335-400 nm. We have attempted to generate the nitrene 51 and/or the related azirine 53, photochemically by direct excitation of the isoxazole 40. However, laser flash photolysis (337.1 nm) of 40 in benzene gives transient absorption phenomena³⁹ having no resemblance to any of those observed in the case of 35a-d. It appears that although the isolation of the isoxazole 40 as a product in the steady-state photolysis indicates the nitrene 51 as a photointermediate, this does not contribute significantly to the absorption spectral changes at 300-400 nm seen in laser flash photolysis. On the basis of the close similarity of the difference absorption spectra as a result of laser excitation with the difference ground-state spectra for cis and trans isomers (see, Figures I.3 and I.4), we conclude that the entire change in absorption at the short wavelengths results from cis-trans photoisomerization of the starting dibenzoylalkenes.⁴⁰

The minor transient species absorbing at long wavelengths (550-700 nm) is best assigned as azomethine ylides (54), formed by the C-C bond cleavage of the aziridine ring (pathway "d"), (Scheme I.8). Little or no reactivity is observed on our time scale for these species towards typical dipolarophiles such as

Scheme 1.8



maleic anhydride and DMAD. However, this is not disturbing because the decay of azomethine ylides, photochemically derived from related aziridines, have been shown⁴¹ to be little affected in the presence of high concentrations (0.8-1.0 M) of dipolarophiles (observed on ~ 100 μ s time scale). The conventional method of observing ylides is steady-state irradiation of the appropriate precursors in a rigid, low temperature matrix. The photolysis (366 nm) of 35a and 35b in EPA glass at 77 K gives rise to colored (green/blue) species with broad absorption spectra ($\lambda_{\text{max}} \approx 620$ and 610 nm), having resemblance to those observed in laser flash photolysis in fluid solutions. The ylide formation is more pronounced in the case of the trans-aziridinyl-dibenzoyl-alkenes; this as well as a possible explanation for the growth process at 420-440 nm will be discussed later.

(Z)-1-Aziridinyl-1,2-dibenzoylalkenes, 36a-d. The laser flash photolysis of substrates 36a-d leads to 'permanent' absorption spectral changes (positive at 300-330 nm and negative at 330-400 nm) that are explainable in terms of trans and cis photoisomerization.⁴⁰ These are indicated in Figure I.5 with 36a as the substrate. In addition, transient species decaying slowly over ~ 100 μ s and showing a broad absorption at long wavelengths (550-700 nm) are formed, particularly in the case of 36a and 36b. A third transient process in the form of a growth component at 400-440 nm occurs at the time scale of the decay of the long-wavelength species (see, the insets D and E of Figure I.5).

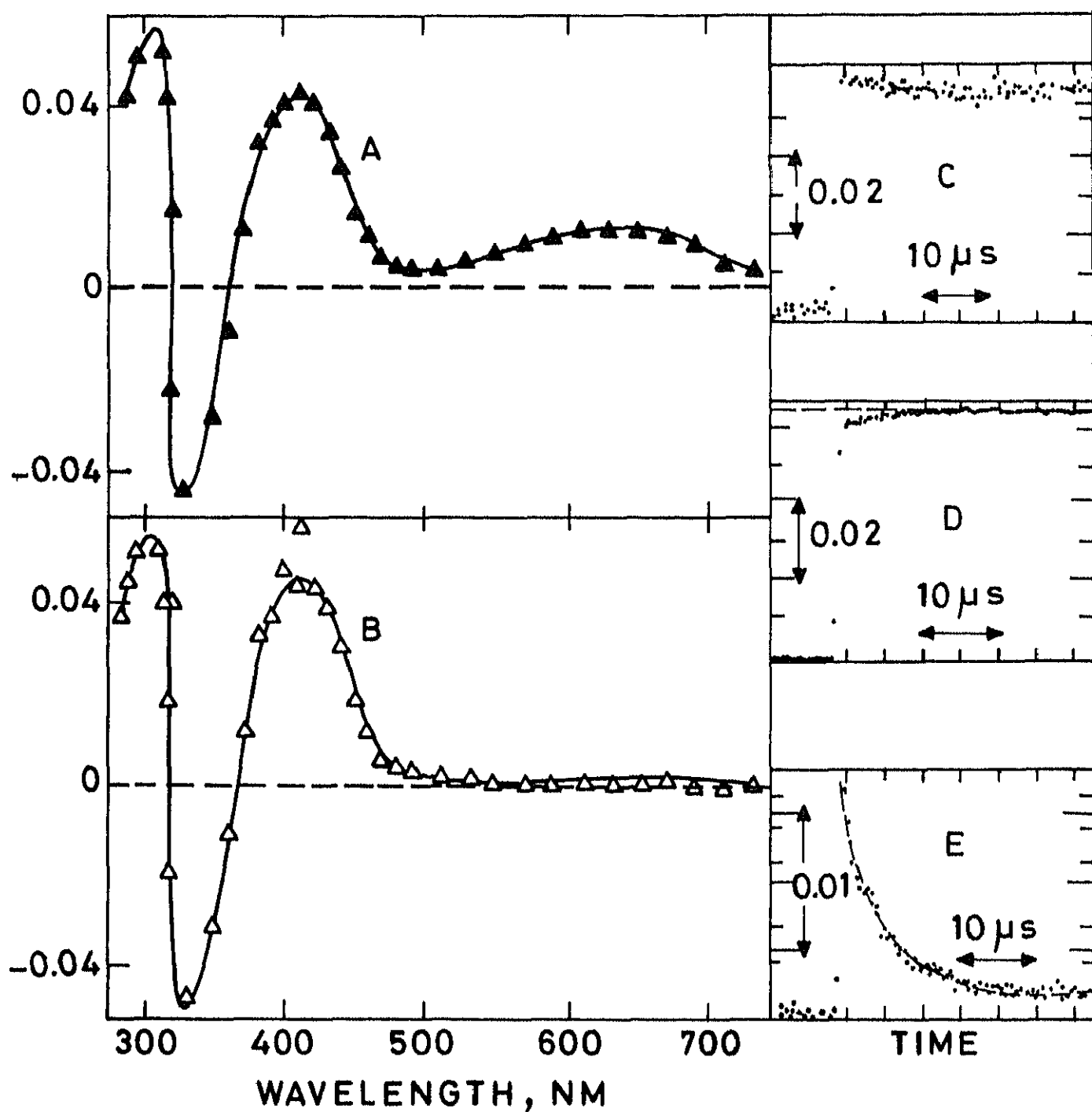


Figure I.5 Transient absorption spectra observed upon 337.1 nm laser flash photolysis of 36b in benzene at 2 μs (A) and 30 μs (B), following the laser flash. Representative kinetic traces at 300 (C), 410 (D) and 640 nm (E) are also shown.

These transient phenomena are analogous to those observed in the case of 35a and 35b, except that the spectral regions of positive and negative absorption changes, dictated by the relative extinction coefficients of cis- and trans-dibenzoylalkenes, are interchanged. Again, oxygen, DTBN and ferrocene show no significant effect on the kinetics and yields of the processes under discussion.

The absorption spectra of the azomethine ylide(s) obtained upon steady-state irradiation (366 nm) of 36a and 36b in EPA glass at 77 K are presented in Figure I.6. The similarity of the two-band spectra (λ_{max} 's = 610 and 605 nm, Figure I.6) with those seen at 400-700 nm in the course of laser flash photolysis (Figure I.4 and Figure I.5) leads us to assign the latter to azomethine ylides. No significant difference in the absorption maxima becomes evident, when one compares the spectra of cis- and trans-aziridinyl-1,2-dibenzoylalkene isomers (35a,b vs 36a,b) or those of cis- and trans-aziridine isomers (35a vs 35b and 36a vs 36b). However, the ease of formation of the ylides from trans-aziridinyl-1,2-dibenzoylethylene isomers (particularly 36a and 36b), relative to their cis-counterparts is noticed under both laser flash and steady-state photolyses.

The fact that the growth processes at 400-440 nm occur in a manner concomitant with that of the decay of ylides (at 600-700 nm) and that the former are absent or negligible for the systems for which ylide formation is also negligible, suggests

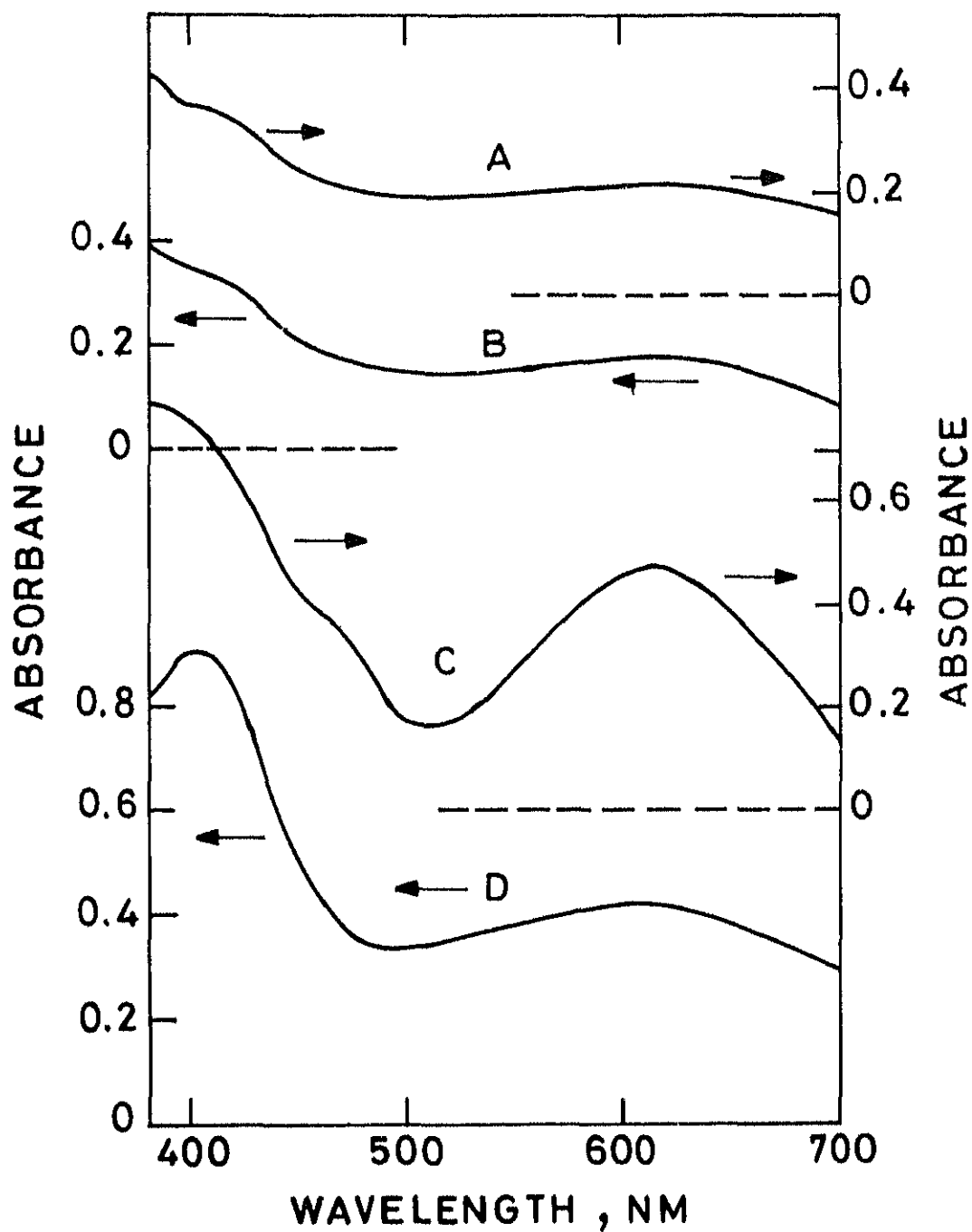


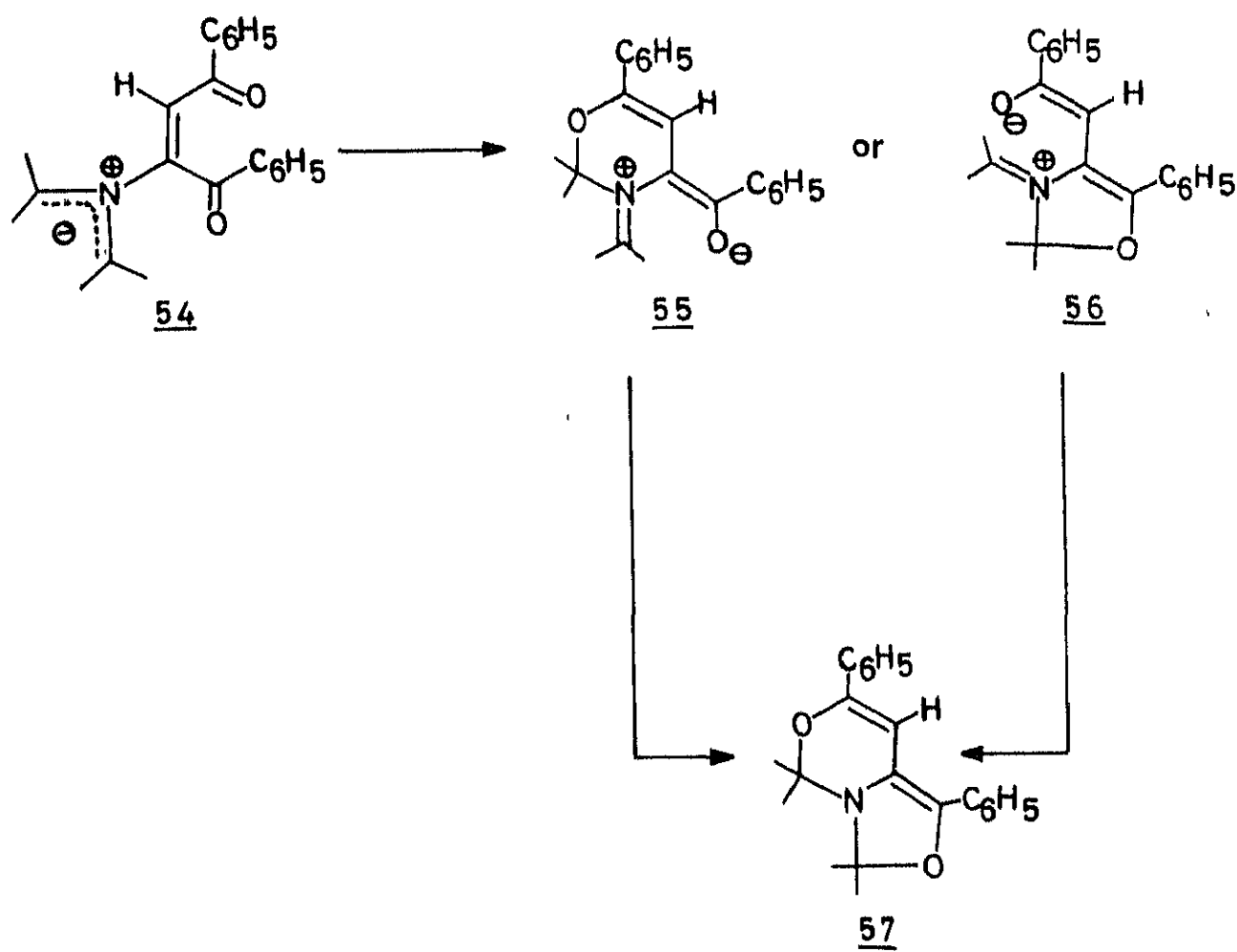
Figure 1.6 Absorption spectra of azomethine ylides upon 366nm photolysis (15–30 min) of 35a (A) 35b (B) 36a (C) and 36b (D) in EPA at 77K .

a precursor/product relationship between them. The most plausible interpretation that comes to our mind is that the ylides undergo further transformation to one or more zwitterionic intermediate(s) (55 and 56) and perhaps leading to the cyclized product 57 (Scheme I.9).

Summary and Conclusions. Laser flash photolysis studies of both 1-aziridinyl-cis-1,2-dibenzoylalkenes (35a-d) and 1-aziridinyl-trans-1,2-dibenzoylalkenes (36a-d) show transient absorption changes which can be explained in terms of cis-trans-photoisomerization and formation of azomethine ylides. These azomethine ylides are also formed by the steady-state irradiation of the starting dibenzoylalkenes in EPA glass at 77 K. In general, it has been observed that the Z isomers (36a-d) are converted to the corresponding azomethine ylides more readily than the corresponding E isomers (35a-d). It is likely that the s-cis or gauche conformer (A, Scheme I.7) of the starting dibenzoylethylenes leads to the pyrroline derivatives 37a-d, whereas the s-trans conformer (B, Scheme I.7) leads to photofragmentation products. These photoprocesses may be taking place through singlet or very short-lived triplet state intermediates.

1.4 EXPERIMENTAL SECTION

All melting points are uncorrected and were determined on a Mel-Temp melting point apparatus. The IR spectra were recorded on Perkin-Elmer Model 377 or Model 580 infrared spectrophoto-

Scheme 1.9

meters. The electronic spectra were recorded on Cary 17D, Cary 219 or Bechman DB spectrophotometers. The ^1H NMR spectra were recorded on a Varian EM-390 or HA-100 NMR spectrometers, using tetramethylsilane as internal standard. The mass spectra were recorded on a Hitachi RMU-GE single-focussing mass spectrometer or a Varian Mat CH7 mass spectrometer at 70 eV. Steady-state irradiations were carried out in a Srinivasan-Griffin Rayonet photochemical reactor (RPR, 3500 Å) or by using a Hanovia 450W medium-pressure mercury lamp in a quartz-jacketed immersion well.

I.4.1 Starting Materials. cis-2,3-Diphenylaziridine (33a),^{42,43} mp 82 °C, trans-2,3-diphenylaziridine (33b),⁴⁴ mp 43-44 °C, cis-2-benzyl-3-phenylaziridine (33c),³⁰ mp 46-47 °C, 2-benzyl-cis-2,3-diphenylaziridine (33d),⁴⁵ mp 86-87 °C and di-benzoylacetylene (DBA, 34),^{46,47} mp 110-111 °C were prepared by reported procedures. Solvents for steady-state photolysis studies were purified and distilled before use, whereas Aldrich Cold Label solvents were used for laser studies. Petroleum ether used was the fraction with bp 60-80 °C.

I.4.2 Preparation of (E)- and (Z)-1-Aziridinyl-1,2-di-benzoylethylenes 35a-d and 36a-d. A general procedure for the preparation of 35a-d and 36a-d was to add a benzene solution of the appropriate aziridine (33a-d, 10 mmol in 25 mL) to a stirred solution of DBA (34, 10 mmol) in benzene (25 mL) at room temperature over 0.5 h and the stirring was continued for an additional

period of 8-10 h. Removal of the solvent under vacuum gave a mixture of products, which was chromatographed on alumina. Elution of the column with petroleum ether gave the Z isomer and further elution with a mixture (1:3) of benzene and petroleum ether gave the E isomer. These adducts were purified by recrystallization from methanol, in each case.

(E)-1-(cis-2,3-Diphenylaziridinyl)-1,2-dibenzoylethylene

(35a). 35a was obtained in 58% yield, mp 146 °C.

IR spectrum ν_{\max} (KBr): 3035 and 2985 (ν_{CH}), 1653 and 1637 ($\nu_{\text{C=O}}$), and 1590 ($\nu_{\text{C=C}}$) cm^{-1} .

UV spectrum λ_{\max} (methanol): 222 nm (ϵ , 35,040), 258 (23,850), and 320 (19,000).

^1H NMR spectrum (CDCl_3): δ 3.80 (d, $J = 1$ Hz, 2 H, methine), 5.70 (s, 1 H, vinylic), and 6.90-7.50 (m, 20 H, aromatic).

Anal. Calcd for $\text{C}_{30}\text{H}_{23}\text{NO}_2$: C, 83.92; H, 5.36; N, 3.26.

Found: C, 83.73; H, 5.18; N, 3.12.

(Z)-1-(cis-2,3-Diphenylaziridinyl)-1,2-dibenzoylethylene

(36a). 36a was obtained in a 29% yield, mp 158 °C.

IR spectrum ν_{\max} (KBr): 3037 and 2984 (ν_{CH}), 1655 and 1635 ($\nu_{\text{C=O}}$), and 1585 ($\nu_{\text{C=C}}$) cm^{-1} .

UV spectrum λ_{\max} (methanol): 218 nm (ϵ , 28,760), 258 (18,020), and 334 (9,590).

^1H NMR spectrum (CDCl_3): δ 3.76 (s, 2 H, methine), 6.32 (s, 1 H, vinylic), and 7.00-7.80 (m, 20 H, aromatic).

Anal. Calcd for $\text{C}_{30}\text{H}_{23}\text{NO}_2$: C, 83.92; H, 5.36; N, 3.26.
Found: C, 83.85; H, 5.19; N, 3.31.

(E)-1-(trans-2,3-Diphenylaziridinyl)-1,2-dibenzoylethylene (35b). 35b was obtained in 50% yield, mp 164 $^\circ\text{C}$.

IR spectrum ν_{max} (KBr): 3055 and 2985 (ν_{CH}), 1660 and 1645 ($\nu_{\text{C=O}}$), and 1593 ($\nu_{\text{C=C}}$) cm^{-1} .

UV spectrum λ_{max} (methanol): 220 nm (ϵ , 24,430), 258 (20,050), and 318 (16,750).

^1H NMR spectrum (CDCl_3): δ 3.85 (s, 2 H, methine), 5.80 (s, 1 H, vinylic), and 7.10-8.10 (m, 20 H, aromatic).

Anal. Calcd for $\text{C}_{30}\text{H}_{23}\text{NO}_2$: C, 83.92; H, 5.36; N, 3.26.
Found: C, 83.59; H, 5.21; N, 3.35.

(Z)-1-(trans-2,3-Diphenylaziridinyl)-1,2-dibenzoylethylene (36b). 36b was obtained in a 30% yield, mp 113 $^\circ\text{C}$.

IR spectrum ν_{max} (KBr): 3041 and 2990 (ν_{CH}), 1650 and 1636 ($\nu_{\text{C=O}}$), and 1589 ($\nu_{\text{C=C}}$) cm^{-1} .

UV spectrum λ_{max} (methanol): 220 nm (ϵ , 17,790), 256 (11,100), and 322 (8,740).

^1H NMR spectrum (CDCl_3): δ 3.80 (s, 2 H, methine), 6.75 (s, 1 H, vinylic), and 7.2-8.0 (m, 2 H, aromatic).

Anal. Calcd for $C_{30}H_{23}NO_2$: C, 83.92; H, 5.36; N, 3.26.

Found: C, 84.12; H, 5.30; N, 3.11.

(E)-1-(cis-2-Benzyl-3-phenylaziridinyl)-1,2-dibenzoylethylene (35c). 35c was obtained in a 43% yield, mp 126 °C.

IR spectrum ν_{\max} (KBr): 3040, 3010, 2986 and 2895 (ν_{CH}), 1660 and 1642 ($\nu_{C=O}$), and 1588 ($\nu_{C=C}$) cm^{-1} .

UV spectrum λ_{\max} (methanol): 222 nm (ϵ , 18,650), 259 (16,990), and 316 (15,680).

1H NMR spectrum ($CDCl_3$): δ 2.50 (m, 2 H, methylene), 2.90 (m, 1 H, methine), 3.80 (d, $J = 5.5$ Hz, 1 H, methine), 6.30 (s, 1 H, vinylic), and 7.10-8.10 (m, 20 H, aromatic).

Anal. Calcd for $C_{31}H_{25}NO_2$: C, 83.79; H, 5.64; N, 3.16.

Found: C, 83.85; H, 5.60; N, 3.46.

(Z)-1-(cis-2-Benzyl-3-phenylaziridinyl)-1,2-dibenzoylethylene (36c). 36c was obtained in a 47% yield, mp 133 °C.

IR spectrum ν_{\max} (KBr): 3050, 3020, 2990 and 2879 (ν_{CH}), 1660 and 1640 ($\nu_{C=O}$), and 1580 ($\nu_{C=C}$) cm^{-1} .

UV spectrum λ_{\max} (methanol): 224 nm (ϵ , 14,920), 256 (10,990), and 324 (9,630).

1H NMR spectrum ($CDCl_3$): δ 2.50 (m, 2 H, methylene), 2.80-3.25 (m, 1 H, methine), 3.55 (d, $J = 5.5$ Hz, 1 H, methine), 6.70 (s, 1 H, vinylic), and 7.10-8.20 (m, 20 H, aromatic).

Anal. Calcd for $C_{31}H_{25}NO_2$: C, 83.97; H, 5.64; N, 3.16.

Found: C, 83.54; H, 5.90; N, 3.29.

(E)-1-(2-Benzyl-cis-2,3-diphenylaziridinyl)-1,2-dibenzoyl-ethylene (35d). 35d was obtained in a 35% yield, mp 176 °C.

IR spectrum ν_{\max} (KBr): 3063, 3044 and 2983 (ν_{CH}), 1665 and 1648 ($\nu_{C=O}$), and 1595 ($\nu_{C=C}$) cm^{-1} .

UV spectrum λ_{\max} (methanol): 220 nm (ϵ , 25,520), 281 (19,300), and 324 (19,330).

1H NMR spectrum ($CDCl_3$): δ 2.80 (q, 2 H, methylene), 3.60 (s, 1 H, methine), 5.80 (s, 1 H, vinylic), and 6.80-8.23 (m, 25 H, aromatic).

Anal. Calcd for $C_{37}H_{29}NO_2$: C, 85.55; H, 5.59; N, 2.70.

Found: C, 85.36; H, 5.48; N, 2.85.

(Z)-1-(2-Benzyl-cis-2,3-diphenylaziridinyl)-1,2-dibenzoyl-ethylene (36d). 36d was obtained in a 48% yield, mp 121-122 °C.

IR spectrum ν_{\max} (KBr): 3065, 3045, 3021 and 2985 (ν_{CH}), 1665 and 1645 ($\nu_{C=O}$), and 1595 ($\nu_{C=C}$) cm^{-1} .

UV spectrum λ_{\max} (methanol): 220 nm (ϵ , 27,020), 258 (20,930), and 332 (9,150).

1H NMR spectrum ($CDCl_3$): δ 2.85 (q, 2 H, methylene), 3.60 (s, 1 H, methine), 6.40 (s, 1 H, vinylic), and 6.80-8.20 (m, 25 H, aromatic).

Anal. Calcd for $C_{37}H_{29}NO_2$: C, 85.55; H, 5.59; N, 2.70.

Found: C, 85.24; H, 5.35; N, 2.81.

I.4.3 Irradiation of (E)-1-(cis-2,3-Diphenylaziridiny)-1,2-dibenzoylethylene (35a). A In Benzene. A solution of 35a (200 mg, 0.47 mmol) in benzene (250 mL) was purged with nitrogen and irradiated (RPR, 3500 Å light source) for 2 h. The irradiation was repeated several times to photolyse, in all, 2.0 g (4.7 mmol) of 35a. Removal of the solvent under vacuum gave a residual solid, which was chromatographed over alumina. Elution with petroleum ether gave 140 mg (17%) of trans-stilbene (39a), mp 124 °C (mixture melting point) and 130 mg (15%) of cis-stilbene (38a), bp 84 °C (@ 4 mm). Further elution with a mixture (1:9) of benzene and petroleum ether gave 35 mg (4%) of 3-benzoyl-5-phenylisoxazole (40), mp 86-87 °C, after recrystallization from methanol (lit.⁴⁸ mp 89 °C). Subsequent elution of the column with a mixture (4:1) of benzene and petroleum ether gave 900 mg (45%) of 2,3-dibenzoyl-cis-4,5-diphenyl- Δ^2 -pyrroline (37a), mp 186 °C, after recrystallization from a mixture (1:1) of methylene dichloride and petroleum ether.

IR spectrum ν_{max} (KBr): 3275 (ν_{NH}), 3088, 3040 and 2990 (ν_{CH}), 1680 and 1665 ($\nu_{\text{C=O}}$), and 1600 ($\nu_{\text{C=C}}$) cm^{-1} .

UV spectrum λ_{max} (methanol): 242 nm (ϵ , 27,500) and 358 (29,200).

Mass spectrum, m/e (relative intensity): 429 (M^+ , 2), 428 ($\text{M}^+ - \text{H}$, 32), 427 ($\text{M}^+ - 2 \text{H}$, 100), 399 ($\text{M}^+ - \text{CO}$, -2H , 40), 351 (4), 350 (45), 324 (28), 322 (3), 249 (4), 248 (11), 234 (4), 195 (2), 194 (9), 180 (19), 105 (73), 103 (3), and 77 (81).

Anal. Calcd for $C_{30}H_{23}NO_2$: C, 83.92; H, 5.36; N, 3.26.

Found: C, 83.95; H, 5.45; N, 3.56.

Air-oxidation of the pyrroline 37a (50 mg, 0.118 mmol) by refluxing in 10 mL of benzene under oxygen saturation for 30 h and workup in the usual manner gave 2,3-dibenzoyl-4,5-diphenylpyrrole (43, 42 mg, 84%), mp 241 °C, after recrystallization from a mixture (1:1) of methylene dichloride and petroleum ether.

IR spectrum ν_{\max} (KBr): 3235 (ν_{NH}), 3075 and 3035 (ν_{CH}), 1670 and 1655 ($\nu_{C=O}$), 1600 and 1585 ($\nu_{C=C}$) cm^{-1} .

UV spectrum λ_{\max} (methanol): 240 nm (ϵ , 33,450), 265 (26,300), and 371 (27,100).

1H NMR spectrum ($CDCl_3$): δ 7.00-8.10 (m, 20 H, aromatic), and 9.20 (broad shoulder, 1 H, D_2O -exchangeable, NH).

B In Methanol. In a repeat run, a solution of 35a (1 g, 2.33 mmol) in methanol (500 mL) was irradiated for 1.5 h (Hanovia 450W, medium pressure mercury lamp with pyrex filter) and worked up as in the earlier case by chromatographing the product mixture over alumina to give 75 mg (18%) of trans-stilbene (39a), mp 124 °C (mixture melting point), 65 mg (15%) of cis-stilbene (38a), bp 84 °C (@ 4 mm), 15 mg (3%) of 40, mp 86-87 °C (mixture melting point), 420 mg (42%) of 37a, mp 186 °C (mixture melting point) and 250 mg (25%) of a polymeric material.

1.4.4 Irradiation of (E)-1-(trans-2,3-Diphenylaziridinyl)-1,2-dibenzoylethylene (35b). A In Benzene. A solution of 35b

(200 mg, 0.47 mmol) in benzene (300 mL) was purged with nitrogen and irradiated (RPR, 3500 Å) for 2 h. The irradiation was repeated several times to photolyse, in all, 2 g (4.7 mmol) of 35b. Removal of the solvent under vacuum gave a residue which was chromatographed over alumina. Elution with petroleum ether gave 135 mg (16%) of trans-stilbene (39a), mp 124 °C (mixture melting point) and 140 mg (17%) of cis-stilbene (38a), bp 84 °C (@ 4 mm). Further elution of the column with a mixture (1:9) of benzene and petroleum ether gave 40 mg (5%) of 40, mp 86-87 °C (mixture melting point).

Subsequent elution of the column with a mixture (4:1) of benzene and petroleum ether gave 880 mg (44%) of 2,3-dibenzoyl-trans-4,5-diphenyl- Δ^2 -pyrroline (37b), mp 207 °C (after recrystallization from a mixture (1:1) of methylene dichloride and petroleum ether).

IR spectrum ν_{max} (KBr): 3275 (ν_{NH}), 3095, 2075, 3035 and 2985 (ν_{CH}), 1680 and 1660 ($\nu_{\text{C=O}}$), 1600 and 1585 ($\nu_{\text{C=C}}$) cm^{-1} .

UV spectrum λ_{max} (methanol): 245 nm (ϵ , 39,350), and 360 (23,500).

Mass spectrum, m/e (relative intensity): 429 (M^+ , 2), 428 ($M^+ - H$, 31), 427 ($M^+ - 2 H$, 100), 399 ($M^+ - CO$, $-2 H$, 43), 351 (5), 350 (39), 324 (31), 322 (4), 249 (3), 248 (11), 234 (5), 195 (5), 194 (13), 180 (17), 105 (71), 103 (5), and 77 (81).

Anal. Calcd for $C_{30}H_{23}NO_2$: C, 83.92; H, 5.36; N, 3.26.
Found: C, 83.95; H, 5.45; N, 3.56.

Elution of the column with a mixture (9:1) of benzene and ethyl acetate gave 350 mg (17%) of a polymeric material, from which no definite product could be isolated.

Air-oxidation of the pyrroline 37b (50 mg, 0.118 mmol) by refluxing in 10 mL of benzene under oxygen saturation for 30 h and workup in the usual manner gave the pyrrole 43 (40 mg, 80%), mp 241 °C (mixture melting point).

B In Methanol. In a repeat experiment, a solution of 35b (1 g, 2.33 mmol) in methanol 500 mL) was irradiated (Hanovia 450W, medium pressure mercury lamp with a pyrex filter) for 1.5 h. Work-up of the mixture as in the earlier case gave 75 mg (18%) of trans-stilbene (39a), mp 124 °C (mixture melting point), 68 mg (16%), of cis-stilbene (38a), bp 84 °C (@ 4 mm), 15 mg (3%) of 40, mp 86-87 °C (mixture melting point), 430 mg (43%) of 37b, mp 207 °C (mixture melting point) and 250 mg (25%) of a polymeric material.

I.4.5 Irradiation of (E)-1-(cis-2-Benzyl-3-phenylaziridinyl)-1,2-dibenzoylethylene (35c). A In Benzene. A benzene solution 35c (200 mg, 0.45 mmol, in 250 mL) was purged with nitrogen and irradiated (RPR, 3500 Å light source) for 2 h. The irradiation was repeated to photolyse, in all, 2 g (4.5 mmol) of 35c. After removal of the solvent under vacuum, the residual solid was chromatographed over alumina. Elution of the column with petroleum ether gave 150 mg (17%) of trans-β-benzylstyrene (39c),

mp 74-75 °C, after recrystallization from methanol.

IR spectrum ν_{\max} (KBr): 3090, 3075, 2925 and 2885 (ν_{CH}), 1575 ($\nu_{\text{C=C}}$) cm^{-1} .

UV spectrum λ_{\max} (methanol): 242 nm (ϵ , 29,550).

^1H NMR spectrum (CDCl_3): δ 3.40 (d, 2 H, methylene), and 6.60-7.30 (m, 12 H, aromatic and vinylic).

Further elution of the column with petroleum ether gave 140 mg (15%) of cis- β -benzylstyrene, mp 41-42 °C, after recrystallization from methanol.

IR spectrum ν_{\max} (KBr): 3090, 3080, 2990, 2927 and 2887 (ν_{CH}), and 1575 ($\nu_{\text{C=C}}$) cm^{-1} .

UV spectrum λ_{\max} (methanol): 235 nm (ϵ , 36,400).

^1H NMR spectrum (CDCl_3): δ 3.30 (d, 2 H, methylene), and 6.70-7.20 (m, 12 H, aromatic and vinylic).

Subsequent elution with a mixture (1:4) of benzene and petroleum ether gave 55 mg (5%) of 40, mp 86-87 °C (mixture melting point).

Further elution of the column with a mixture (1:1) of benzene and petroleum ether gave 900 mg (45%) of 5-benzyl-2,3-dibenzoyl-4-phenyl- Δ^2 -pyrroline (37), mp 194 °C, after recrystallization from a mixture (1:1) of methylene dichloride and petroleum ether.

IR spectrum ν_{\max} (KBr): 3260 (ν_{CH}), 3080, 3030 and 2975 (ν_{CH}), 1685 and 1665 ($\nu_{\text{C=O}}$), and 1600 ($\nu_{\text{C=C}}$) cm^{-1} .

UV spectrum λ_{max} (Methanol): 246 nm (ϵ , 33,500), and 352 (22,100).

Mass spectrum, m/e (relative intensity): 443 (M^+ , 2), 441 ($M^+ - 2 \text{ H}$, 54), 366 ($M^+ - \text{C}_6\text{H}_5$, 1), 365 ($M^+ - \text{H}$, $-\text{C}_6\text{H}_5$, 24), 364 (54), 351 (2), 338 ($M^+ - \text{COC}_6\text{H}_5$, 5), 336 ($M^+ - 2 \text{ H}$, $-\text{COC}_6\text{H}_5$, 11), 259 (5), 248 (9), 234 (2), 209 (11), 207 (11), 194 (18), 192 (7), 105 (100), and 91 (44).

Anal. Calcd for $\text{C}_{31}\text{H}_{25}\text{NO}_2$: C, 83.97; H, 5.64; N, 3.16.
Found: C, 83.81; H, 5.60; N, 3.21.

Further elution of the column with a mixture (9:1) of ethyl acetate and benzene gave 400 mg (20%) of a polymeric material.

Air-oxidation of 37c gave 5-benzyl-2,3-dibenzoyl-4-phenylpyrrole (48), mp 217 °C, after recrystallization from methanol.

IR spectrum ν_{max} (KBr). 3255 (ν_{NH}), 3075 and 2945 (ν_{CH}), 1655 and 1645 ($\nu_{\text{C=O}}$), and 1600 ($\nu_{\text{C=C}}$) cm^{-1} .

UV spectrum λ_{max} (methanol): 243 nm (ϵ , 36,500), and 369 (25,700).

^1H NMR spectrum (CDCl_3): δ 3.40 (s, 2 H, methylene), 7.20-8.30 (m, 20 H, aromatic), and 8.60 (s, 1 H, D_2O -exchangeable, NH).

Anal. Calcd for $\text{C}_{31}\text{H}_{23}\text{NO}_2$: C, 84.35; H, 5.22; N, 3.17.
Found: C, 84.16; H, 5.34; N, 3.24.

B In Methanol. In a repeat experiment, a solution of 35c (1 g, 2.25 mmol) in methanol (500 mL) was irradiated (Hanovia 450W medium pressure mercury lamp with pyrex filter) for 1.5 h

and worked up as in the earlier case to give 90 mg (21%) of 39c, mp 74-75 °C (mixture melting point), 65 mg (18%) of 38c, mp 41-42 °C (mixture melting point), 24 mg (4%) of 40, mp 86-87 °C (mixture melting point), 455 mg (46%) of 37c, mp 194 °C (mixture melting point), and 180 mg (18%) of a polymeric material.

I.4.6 Irradiation of (E)-1-(2-Benzyl-cis-2,3-diphenyl-aziridinyl-1,2-dibenzoyl)ethylene (35d). A In Benzene. A solution of 35d (200 mg, 0.38 mmol) in benzene (250 mL) was purged with nitrogen and irradiated (PPR, 3500 Å lamp source) for 2 h. The irradiation was repeated several times to photolyse, in all, 2 g (3.85 mmol) of 35d. Removal of the solvent under vacuum from the combined photolysates gave a residual solid which was chromatographed over neutral alumina. Elution with petroleum ether gave 250 mg (30%) of trans-β-benzylstilbene (39a), mp 133 °C, after recrystallization from methanol.

IR spectrum ν_{\max} (KBr): 3078, 3055, 2984 and 2875 (ν_{CH}), 1586 ($\nu_{\text{C=C}}$) cm^{-1} .

UV spectrum λ_{\max} (Methanol): 291 nm (ϵ , 23,200).

^1H NMR spectrum (CDCl_3): δ 3.60 (s, 2 H, methylene), 7.2-8.3 (m, 16 H, aromatic and vinylic).

Anal. Calcd for $\text{C}_{27}\text{H}_{18}$: C, 93.33; H, 6.67. Found: C, 93.51; H, 6.55.

Further elution with petroleum ether gave 290 mg (35%) of cis-β-benzylstilbene (38d), mp 79-80 °C, after recrystallization

from methanol.

IR spectrum ν_{\max} (KBr): 3082, 3052, 2980 and 2872 (ν_{CH}), and 1584 ($\nu_{\text{C}=\text{C}}$).

UV spectrum λ_{\max} (methanol): 286 nm (ϵ , 23,400).

^1H NMR spectrum (CDCl_3): δ 3.40 (s, 2 H, methylene), and 7.10-8.30 (m, 16 H, aromatic and vinylic).

Anal. Calcd for $\text{C}_{27}\text{H}_{18}$: C, 93.33; H, 6.67. Found: C, 93.61; H, 6.38.

Subsequent elution of the column with a mixture (1:4) of benzene and petroleum ether gave 105 mg (11%) of 40, mp 86-87 °C (mixture melting point), after recrystallization from methanol.

Further elution with a mixture (1:1) of benzene and petroleum ether gave 200 mg (10%) of 5-benzyl-2,3-dibenzoyl-cis-4,5-diphenyl- Δ^2 -pyrroline (37d), mp 211 °C, after recrystallization from a mixture (1:1) of methylene dichloride and petroleum ether.

IR spectrum ν_{\max} (KBr): 3245 (ν_{NH}), 3091, 3085, 3025, 2975 and 2845 (ν_{CH}), 1665 and 1645 ($\nu_{\text{C}=\text{O}}$), and 1600 ($\nu_{\text{C}=\text{C}}$) cm^{-1} .

UV spectrum λ_{\max} (methanol): 240 nm (ϵ , 34,350), and 360 (21,600).

^1H NMR spectrum (CDCl_3): δ 2.80 (q, 2 H, methylene), 3.54 (s, 1 H, methine), and 6.80 (broad s, 1 H, D_2O -exchangeable, NH), 7.10-8.10 (m, 25 H, aromatic).

Anal. Calcd for $C_{37}H_{29}NO_2$: C, 85.55; H, 5.59; N, 2.70.
Found: C, 85.83; H, 5.48; N, 2.86.

Further elution of the column with methanol gave 400 mg (20%) of a polymeric material.

B In Methanol. In a repeat experiment, a solution of 35d (1 g, 1.89 mmol) in methanol (500 mL) was irradiated (Hanovia 450W medium pressure mercury lamp with pyrex filter) for 1.5 h and worked up as in the earlier case to give 120 mg (29%) of 39d, mp 133 °C (mixture melting point), 140 mg (32%) of 38d, mp 79-80 °C (mixture melting point), 60 mg (13%) of 40, mp 86-87 °C (mixture melting point), 75 mg (8%) of 37d, mp 211 °C (mixture melting point), and 250 mg (25%) of a polymeric material.

I.4.7 Irradiation of (Z)-1-Aziridinyl-1,2-dibenzoyl-alkenes (36a-d). A general procedure was to irradiate a solution of the Z isomers (36a-d, 2-3 mmol) in benzene (500 mL) under a Hanovia 450W medium pressure mercury lamp source for a period of 2.0-2.5 h. After removal of the solvent under reduced pressure, the residual solid was chromatographed over alumina. Elution of the column with petroleum ether gave a mixture of the trans- and cis-ethylene derivatives, which could be separated and purified by fractional crystallization from methanol. Subsequent elution of the column with a mixture (1:9) of benzene and petroleum ether gave the unchanged starting material (Z isomers). Further elution with a mixture (1:4) of benzene and petroleum ether gave the E isomers (35a-d). Continued elution of the column with a mixture

Irradiation of 36a. 36a (1 g, 2.33 mmol) was irradiated for 2 h and worked up to give 45 mg (10%) of 39a, mp 124 °C (mixture melting point), 35 mg (8%) of 38a, bp 84 °C (@ 4 mm), 220 mg (22%) of 36a, mp 158 °C (mixture melting point), 300 mg (30%) of the E isomer 35a, mp 146 °C (mixture melting point, 110 mg (11%) of the pyrroline 37a, mp 186 °C (mixture melting point) and 150 mg (15%) of a polymeric material.

Irradiation of 36b. Irradiation of 36b (1 g, 2.33 mmol) for 2 h and workup of the reaction mixture gave 35 mg (8%) of 39a, mp 124 °C (mixture melting point), 40 mg (9%) of 38a, bp 84 °C (@ 4 mm), 200 mg (20%) of the unchanged starting material (36b), mp 113 °C (mixture melting point), 330 mg (33%) of the E isomer, 35b, mp 164 °C (mixture melting point), 130 mg (13%) of the pyrroline derivative 37a, mp 207 °C (mixture melting point) and 150 mg (15%) of a polymeric material.

Irradiation of 36c. 36c (1 g, 2.25 mmol) was photolysed for 2.5 h and worked up to give 30 mg (7%) of 39c, mp 74-75 °C (mixture melting point), 25 mg (6%) of 38c, mp 41-42 °C (mixture melting point), 180 mg (18%) of the unchanged starting material 36c, mp 133 °C (mixture melting point), 350 mg (35%) of the E isomer 35c, mp 126 °C (mixture melting point), 120 mg (12%) of the pyrroline 37c, mp 194 °C (mixture melting point), and 150 mg (15%) of a polymeric material.

Irradiation of 36d. Irradiation of 36d (1 g, 1.98 mmol) for 2.5 h gave 70 mg (17%) of 39d, mp 130-131 °C (mixture melting

point), 65 mg (16%) of 38d, mp 79-80 °C (mixture melting point), 100 mg (10%) of the unchanged starting material 36d, mp 120-121 °C (mixture melting point), 28 mg (3%) of 40, mp 86-87 °C (mixture melting point), 200 mg (20%) of the E isomer 35d, mp 176 °C (mixture melting point), 40 mg (4%) of the pyrroline 37d, mp 211 °C (mixture melting point), and 180 mg (18%) of a polymeric material.

1.4.8 Thermolysis of 37a in Diphenyl Ether (DPE). A solution of 37a (500 mg, 1.16 mmol) in DPE (10 mL) was heated around 255 °C for 1 h. Removal of the solvent under vacuum gave a residual solid, which was chromatographed over silica gel. Elution of the column with a mixture (1:2) of benzene and petroleum ether gave 125 mg (26%) of 3-benzoyl-2,4,5-triphenylpyrrole (44), mp 203 °C, after recrystallization from a mixture (1:1) of benzene and petroleum ether.

IR spectrum ν_{\max} (KBr): 3226 (ν_{NH}), 3085 and 3045 (ν_{CH}), 1665 ($\nu_{\text{C=O}}$), and 1600 and 1585 ($\nu_{\text{C=C}}$) cm^{-1} .

UV spectrum λ_{\max} (methanol): 235 nm (ϵ , 29,300), and 276 (26,700).

^1H NMR spectrum (CDCl_3): δ 6.80-8.10 (m, 20 H, aromatic) and 9.30 (broad s, 1 H, D_2O -exchangeable, NH).

Mass spectrum, m/e (relative intensity): 399 (M^+ , 3), 398 (20), 322 (5), 321 (2), 294 (8), 293 (3), 221 (17), 220 (2), 206 (11), 195 (48), 193 (13), 178 (27), 105 (100), 103 (2) and 77 (93).

Anal. Calcd for $C_{29}H_{21}NO$: C, 87.22; H, 5.26; N, 3.51.

Found: C, 87.41; H, 5.34; N, 3.50.

Further elution of the column with a mixture (1:1) of benzene and petroleum ether gave 270 mg (54%) of 2,3-dibenzoyl-4,5-diphenylpyrrole (43), mp 241 °C (mixture melting point), after recrystallization from a mixture (1:1) of methylene dichloride and petroleum ether.

I.4.9 Thermolysis of 37b in DPE. A solution of 37b (500 mg, 1.16 mmol) in DPE (10 mL) was heated around 255 °C for 1 h and the reaction mixture was worked up as in the earlier case to give 140 mg (30%) of 44, mp 203 °C (mixture melting point) and 255 mg (51%) of 43, mp 241 °C (mixture melting point).

1.4.10 Preparation of 43 from 46. To a stirred slurry of 46²⁸ (500 mg, 0.16 mmol) in petroleum ether (15 mL) was added phosphorous trichloride (545 mg, 0.40 mmol) over 5 minutes at room temperature and the reaction mixture was then refluxed for 1 h. Removal of the solvent under reduced pressure gave the crude diacyl chloride, which was dissolved in benzene (15 mL). This solution was then gradually added to a stirred slurry of aluminium chloride (530 mg, 0.4 mmol) in benzene (25 mL) at 5 °C. The reaction mixture was stirred at room temperature (~25 °C) for 3 h and worked up by pouring over crushed ice and extraction with benzene. Removal of the solvent under vacuum gave 550 mg (78%) of 43, mp 239-240 °C (mixture melting point), after recrystallization from a mixture (1:1) of methylene dichloride and petroleum ether.

I.4.11 Preparation of 44 from 47. Treatment of 47²⁹

(500 mg, 0.15 mmol) with phosphorous trichloride (265 mg, 0.20 mmol) as in the earlier case gave the corresponding acyl chloride, which was subsequently treated with benzene in presence of aluminium chloride to give 450 mg (79%) of 44, mp 201-202 °C (mixture melting point, after recrystallization from a mixture (1:1) of methylene dichloride and petroleum ether.

I.4.12 Laser Flash Photolysis.³⁸ Pulse excitation was

carried out at 337.1 nm (2-3 mJ, ~ 8 ns), employing a UV 400 Molelectron Nitrogen laser. The transient phenomena were observed in 3 x 7 mm quartz cells using a kinetic spectrometer, described elsewhere.⁴⁹ The solvents employed were benzene and methanol and unless oxygen effects were meant to be studied, the solutions were deoxygenated by purging with argon or nitrogen. In the experiments where a large number of laser shots were necessary, e.g., for wavelength-by-wavelength measurements of transient absorption spectra, a flow system was used in which the solution for photolysis was allowed to drain from a reservoir through the cell.

I.5 REFERENCES

- (1) G. W. Griffin and E. J. O'Connell, J. Am. Chem. Soc. 84, 4148-4149 (1962).
- (2) H. E. Zimmerman, H. G. C. Durr, R. G. Lewis and S. Braun, J. Am. Chem. Soc. 84, 4149-4150 (1962).
- (3) H. E. Zimmerman, H. G. C. Durr, R. G. Givens and R. S. Lewis, J. Am. Chem. Soc. 89, 1863-1874 (1967).
- (4) A. Padwa, D. Crumrine and A. Schubber, J. Am. Chem. Soc. 88, 3064-3069 (1966).
- (5) N. Sugiyama and C. Kashima, Bull. Chem. Soc. Jpn. 43, 1875-1877 (1970).
- (6) S. Lahiri, V. Dabral, S. M. S. Chauhan, E. Chackachery, C. V. Kumar, J. C. Scaiano and M. V. George, J. Org. Chem. 45, 3782-3790 (1980).
- (7) C. V. Kumar, B. A. R. C. Murty, S. Lahiri, E. Chackachery, J. C. Scaiano and M. V. George, J. Org. Chem. 49, 4923-4929 (1984).
- (8) C. V. Kumar, Ph.D. Thesis, Indian Institute of Technology, Kanpur, 1981.
- (9) B. A. R. C. Murty, C. V. Kumar, V. Dabral, P. K. Das and M. V. George, J. Org. Chem. 49, 4165-4171 (1984).
- (10) B. A. R. C. Murty, Ph.D. Thesis, Indian Institute of Technology, Kanpur, 1982.
- (11) B. A. R. C. Murty, S. Pratapan, C. V. Kumar, P. K. Das and M. V. George, J. Org. Chem. 50, 2533-2538 (1985).

- (12) B. B. Lohray, C. V. Kumar, P. K. Das and M. V. George, J. Org. Chem. 49, 4647-4656-(1984).
- (13) B. B. Lohray, Ph.D. Thesis, Indian Institute of Technology, Kanpur, 1982.
- (14) H. E. Zimmerman, In "Rearrangements in Ground and Excited States," P. de Mayo, Ed., Academic Press: New York, Vol. 3, pp. 131-166 (1980).
- (15) N. R. Bertoniere and G. W. Griffin, "Organic Photochemistry," O. L. Chapman, Ed., Marcell Dekker: New York, Vol. 3, pp. 115-195 (1973).
- (16) M. Nastasi and J. Streith, In "Rearrangements in Ground and Excited States," P. de Mayo, Ed., Academic Press: New York, Vol. 3, pp. 445-499 (1980).
- (17) S. T. Reid, In "Advances in Heterocyclic Chemistry," A. R. Katritzky, Ed., Academic Press: New York, Vol. 30, pp. 239-317 (1982).
- (18) R. Huisgen, W. Scheer and H. Huber, J. Am. Chem. Soc. 89, 1753-1755 (1967).
- (19) H. Hermann, R. Huisgen and H. Mäder, J. Am. Chem. Soc., 93, 1779-1780 (1971).
- (20) A. Padwa and W. Eisenhardt, J. Am. Chem. Soc. 90, 2442-2444 (1968).
- (21) A. Padwa, W. Eisenhardt, J. Am. Chem. Soc. 93, 1400-1408 (1971).
- (22) A. Padwa, D. Dean and T. Oline, J. Am. Chem. Soc. 97, 2822-2829 (1975).

- (23) A. G. Anastassiou and R. B. Hamner, J. Am. Chem. Soc. 94, 303-305 (1972).
- (24) (a) K. Herbig, R. Huisgen and H. Huber, Chem. Ber. 99, 2546-2555 (1966); (b) S. Lahiri, M. P. Mahajan, R. Prasad and M. V. George, Tetrahedron 33, 3159-3170 (1970).
- (25) J. E. Dolfini, J. Org. Chem. 30, 1298-1301 (1965).
- (26) W. E. Truce and D. G. Brady, J. Org. Chem. 31, 3543-3546 (1966).
- (27) R. Huisgen, B. Giese and H. Huber, Tetrahedron Lett., 1883-1885 (1967).
- (28) K. Yamamoto, T. Hattori and K. Kariyone, J. Pharm. Soc. Jpn. 75, 1219-1223 (1955).
- (29) V. Sprio and P. Madonia, Gazz. Chim. Ital. 87, 171-180 (1957); Chem. Abstr. 52, 15501b (1957).
- (30) K. Kitahonoki, K. Kotera, Y. Matsukawa, S. Miyazaki, T. Okada, H. Takahashi and Y. Takano, Tetrahedron Lett. 1059-1065 (1965).
- (31) For some examples of vinylcyclopropane rearrangements, see, R. N. Warrner and J. B. Bremner, Rev. Pure Appl. Chem. 16, 117 (1966).
- (32) For some examples of the photorearrangements of cyclopropyl olefinic esters, see, (a) M. J. Jorgenson and C. H. Heathcock, J. Am. Chem. Soc. 87, 5264-5266 (1965); (b) M. J. Jorgenson, J. Am. Chem. Soc. 88, 3463-3464 (1966); (c) M. J. Jorgenson, J. Am. Chem. Soc. 91, 6432-6443 (1969).
- (33) G. R. De Mare and J. S. Martin, J. Am. Chem. Soc. 88, 5033-5034 (1966).

- (34) S. Sarel, J. Yovell and M. Sarel-Imber, *Angew. Chem.* 80, 592-603 (1968).
- (35) A. Padwa, *Acc. Chem. Res.* 4, 48-57 (1971).
- (36) A. Padwa and L. Hamilton, *J. Am. Chem. Soc.* 89, 102-112 (1967).
- (37) (a) W. Schäfer, H. E. Moore and A. Aguado, *Synthesis*, 30-32 (1974); (b) R. Neidlein, G. Humburg, A. Given and C. Hahn, *Chem. Ber.* 111, 3346-3353 (1978); (c) K. Isomura, Y. Hirose, H. Shuyama, S. Abe, G. Ayabe and H. Taniguchi, *Heterocycles* 9, 1207 (1978).
- (38) All laser flash photolysis studies have been carried out by Dr. P. K. Das, Dr. C. V. Kumar and Professor M. V. George at the Radiation Laboratory of the University of Notre Dame (USA).
- (39) The laser flash photolysis of the isoxazole 40 in benzene leads to the formation of a transient that is best assigned as a nitrile ylide. The details of these studies will be published elsewhere.
- (40) That photoisomerization occurs is shown by the isolation of cis-isomers upon steady-state photolysis of the trans-dibenzoylethylenes. The photolysis conditions (350 nm) were such that the trans-isomers absorbed the light preferentially.
- (41) K. Bhattacharyya, D. Ramiah, P. K. Das and M. V. George, *J. Phys. Chem.* 90, 3221-3229 (1986).

- (42) A. Hassner and G. E. Galle, *J. Am. Chem. Soc.* 92, 3733-3739 (1970).
- (43) A. Hassner, C. J. Mathews and W. Fowler, *J. Am. Chem. Soc.* 91, 5046-5054 (1969).
- (44) T. A. Foglia and D. Swern, *J. Org. Chem.* 32, 75-78 (1967).
- (45) K. Kotera, Y. Takano, A. Matsuura and K. Kitahonoki, *Tetrahedron* 26, 539-556 (1970).
- (46) R. E. Lutz and W. R. Smithy, *J. Org. Chem.* 16, 51-56 (1951).
- (47) R. E. Lutz 'Organic Synthesis,' E. C. Horning, Ed. John Wiley and Sons, Inc., New York, Col. Vol. 3, pp. 248-250 (1955).
- (48) V. S. Cusmano, *Gazz. Chim. Ital.* 79, 622-630 (1948); *Chem. Abstr.* 43, 2991h (1948).
- (49) (a) P. K. Das, M. V. Erucinas, Jr., R. D. Small and J. C. Scaiano, *J. Am. Chem. Soc.* 101, 6965-6970 (1979); (b) P. K. Das and K. Bobrowski, *J. Chem. Soc., Faraday Trans. 2*, 77, 1009-1027 (1981); (c) S. K. Chattopadhyay, P. K. Das and G. Hug, *J. Am. Chem. Soc.* 104, 4507-4514 (1982).

CHAPTER II

PHOTOTRANSFORMATIONS OF 1-IMIDAZOLYL- 1,2-DIBENZOYLALKENES

II.1 ABSTRACT

The photochemistry of a number of 1-imidazolyl-1,2-dibenzoylalkenes has been investigated through steady-state photolysis. Laser flash photolysis experiments have been carried out to study the transients involved in these photoreactions and thereby to understand the mechanistic details. The substrates that we have examined in the present studies include (E)-1-(2,4,5-triphenylimidazolyl)-1,2-dibenzoylethylene (3a), (E)-1-(4,5-diphenylimidazolyl)-1,2-dibenzoylethylene (3b), (E)-1-(4,5-dimethyl-2-phenylimidazolyl)-1,2-dibenzoylethylene (3c), (E)-1-(2-phenylbenzimidazolyl)-1,2-dibenzoylethylene (3d), (E)-1-benzimidazolyl-1,2-dibenzoylethylene (3e) and (Z)-1-(2-phenylbenzimidazolyl)-1,2-dibenzoylethylene (4d).

Product analysis revealed that several photoreactions are involved in the transformations of 1-imidazolyl-1,2-dibenzoylalkenes, depending on the substituents present in the

imidazolyl moieties. These include intramolecular phenyl group migration leading to ketene-mediated 3-butenic acids or esters, electrocyclic ring-closure reactions leading to dihydrophenanthrene and dihydroisoquinoline derivatives and also photofragmentation reactions resulting in the loss of imidazolyl moieties from the parent dibenzoylalkenes. Laser flash photolysis in several cases gave rise to transient processes attributable to ketene and zwitterionic intermediates. Reasonable mechanisms have been suggested to account for the different products formed in these photoreactions.

II.2 INTRODUCTION

Photorearrangements of 1,2-dibenzoylalkenes are known to give a variety of products, depending on the nature of substituents present in them.¹⁻⁶ The phototransformations of several substrates containing 1,2-dibenzoylalkene moieties such as 1,4- and 1,2-epoxy compounds,^{7,8} dibenzobarrelenes,⁹⁻¹¹ 1-pyrazolyl-1,2-dibenzoylalkenes,^{12,13} and 1-aziridinyl-1,2-dibenzoylalkenes¹⁴ have been reported recently from this laboratory. The object of the present investigation has been to examine the phototransformations of selected 1-imidazolyl-1,2-dibenzoylalkenes and 1-benzimidazolyl-1,2-dibenzoylalkenes containing suitably positioned substituents which are capable of undergoing other types of photoreactions, besides the 1,2-dibenzoylalkene rearrangement. In addition, laser flash photolysis studies have been carried out to characterize the transients

involved in these photoreactions. Some of the substrates that we have examined in this study include (E)-1-(2,4,5-triphenylimidazolyl)-1,2-dibenzoylethylene (3a), (E)-1-(4,5-diphenylimidazolyl)-1,2-dibenzoylethylene (3b), (E)-1-(4,5-dimethyl-2-phenylimidazolyl)-1,2-dibenzoylethylene (3c), (E)-1-(2-phenylbenzimidazolyl)-1,2-dibenzoylethylene (3d), (E)-1-benzimidazolyl-1,2-dibenzoylethylene (3e), and (Z)-1-(2-phenylbenzimidazolyl)-1,2-dibenzoylethylene (4d).

In principle, the photoreactions of (E)-1-imidazolyl-1,2-dibenzoylethylenes (3a-e) should follow two distinct pathways, one involving the reactions of the imidazolyl component and the other relating to the dibenzoylalkene fragment. In addition, substrates such as 3a and 3b containing cis-stilbene moieties should be capable of undergoing electrocyclic ring-closure reactions leading to dihydrophenanthrene derivatives. Substrates such as 3a, 3c and 3d, bearing a phenyl substituent at the C-2 position of the imidazolyl moiety should, on the other hand, be capable of undergoing electrocyclic ring-closure reactions, incorporating the phenyl substituent and the 1,2-dibenzoylalkene fragment, leading to imidazolo[2,1-a]-5,6-dihydroisoquinoline derivatives, besides other reactions.

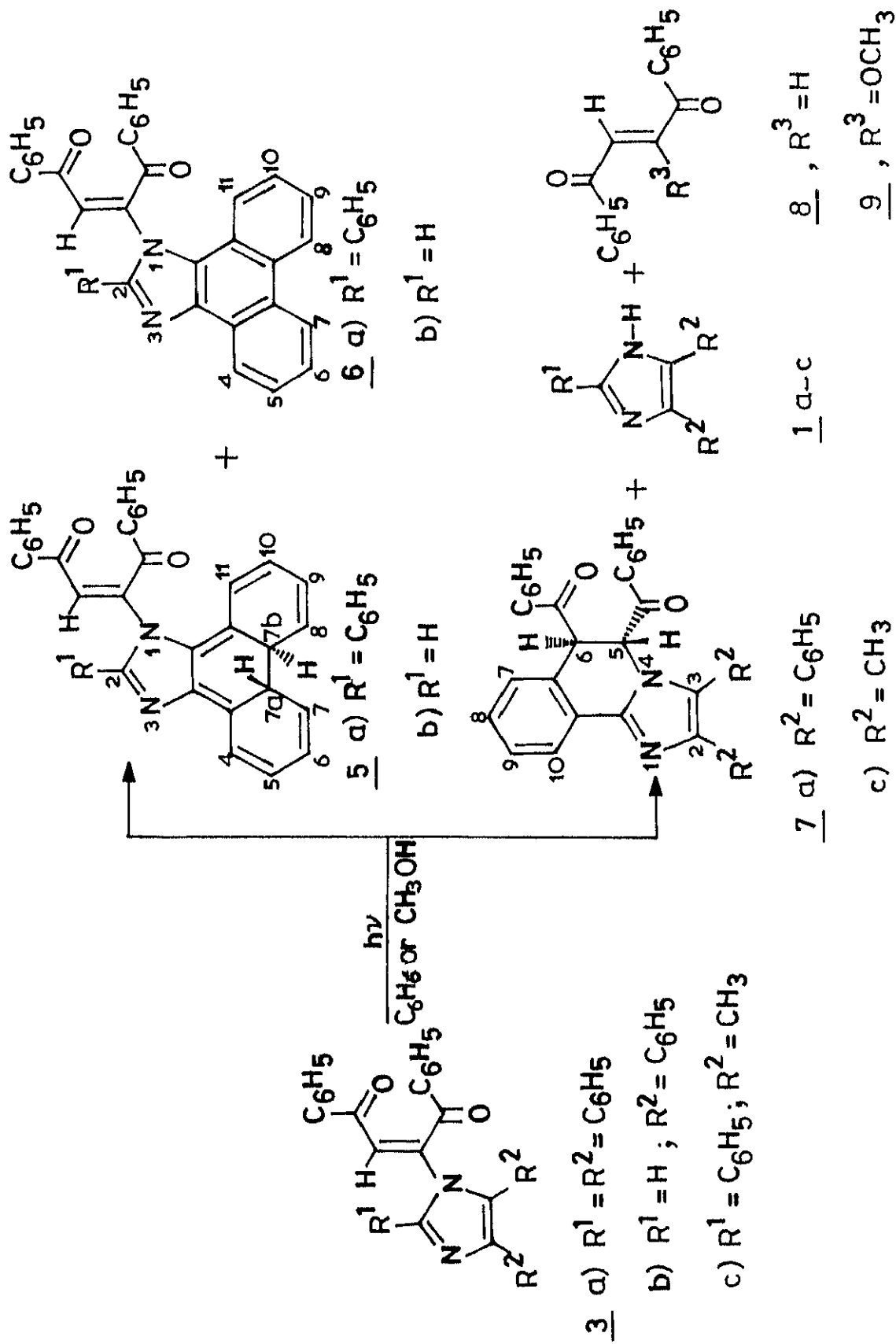
II.3 RESULTS AND DISCUSSION

II.3.1 Preparation of Starting Materials. We have prepared the (E)-1-imidazolyl-1,2-dibenzoylalkenes, 3a-e and the corresponding Z isomers, 4a-e in yields ranging between 66-82%

and 6-35%, respectively, through the reaction of the appropriate imidazoles, 1a-e with dibenzoylacetylene (DBA, 2) in refluxing acetonitrile (Scheme II.1). The structures of all these adducts were determined on the basis of analytical results and spectral data, whereas, the geometry across the carbon-carbon double bond has been ascertained on the basis of their electronic spectra.¹⁴⁻¹⁷ The E isomers 3a-e show an absorption maximum, in each case, around 250-271 nm, with relatively lower extinction coefficients, whereas the Z isomers 4a-e absorb around 260-280 nm with higher extinction coefficients.

II.3.2 Preparative Photochemistry and Product Identification. Irradiation of 3a in benzene gave a 18% yield of threo-5,6-dibenzoyl-2,3-diphenylimidazolo[2,1-a]-5,6-dihydroisoquinoline (7a), 22% yield of (E)-1-(7a,7b-dihydrophenanthro[9,10-d]-2-phenylimidazolyl)-1,2-dibenzoylethylene (5a), 20% yield of (E)-1-(phenanthro[9,10-d]-2-phenylimidazolyl)-1,2-dibenzoylethylene (6a), 17% yield of 2,4,5-triphenylimidazole (1a), and a 6% yield of trans-1,2-dibenzoylethylene (8) (Scheme II.2). Similarly, the irradiation of 3a in methanol gave a mixture of 7a (10%), 5a (15%), 6a (25%), 1a (34%), and trans-1-methoxy-1,2-dibenzoylethylene (9, 14%). The structures of 5a, 6a and 7a have been determined on the basis of analytical results and spectral data, whereas the structures of 1, 8 and 9 were confirmed by comparing their melting points and mixture melting points with authentic samples.

Scheme II.2



The ^1H NMR spectrum of 5a, for example, showed a doublet of a doublet at ~~ca~~ δ 2.45 (1 H, $J_{7a,7b} = 18$ Hz, $J_{7,7a} = 4.5$ Hz), assigned to the C-7b proton and a second doublet of a doublet at δ 3.25 (1 H, $J_{7a,7b} = 18$ Hz, $J_{7b,8} = 6.5$ Hz), assigned to the C-7b proton. The protons at C-7 and C-8 positions appeared as two quartets at δ 5.15 (1 H) and δ 6.65 (1 H), respectively, whereas the aromatic and vinylic protons appeared as a complex multiplet centered at δ 8.0 (22 H) (Figure II.2). On the other hand, the ^1H NMR spectrum of 6a showed a multiplet spread over the region at δ 6.95-8.85, assigned to the aromatic and vinylic protons (Figure II.3).

Further confirmation on the structures of 5a and 6a was derived through the air-oxidation of 5a in refluxing benzene to give a 81% yield of 6a.

The ^1H NMR spectrum of 7a showed a doublet at δ 3.05 (1 H, $J = 15$ Hz), assigned to the C-6 protons and another doublet at δ 4.35 (1 H, $J = 15$ Hz), assigned to the C-5 proton. The aromatic protons appeared as a multiplet centered around δ 7.75 (24 H) (Figure II.4). The relatively high coupling constant of 15 Hz ($J_{5,6}$) indicates that the C-5 and C-6 protons in 7a are anti with respect to each other as would be the case with the threo isomer.

Similarly, the irradiation of 3b in benzene gave a mixture of (E)-1-(7a,7b-dihydrophenanthro[9,10-d]imidazolyl)-1,2-dibenzoylethylene (5b, 24%), (E)-1-(phenanthro[9,10-d]imidazolyl)-

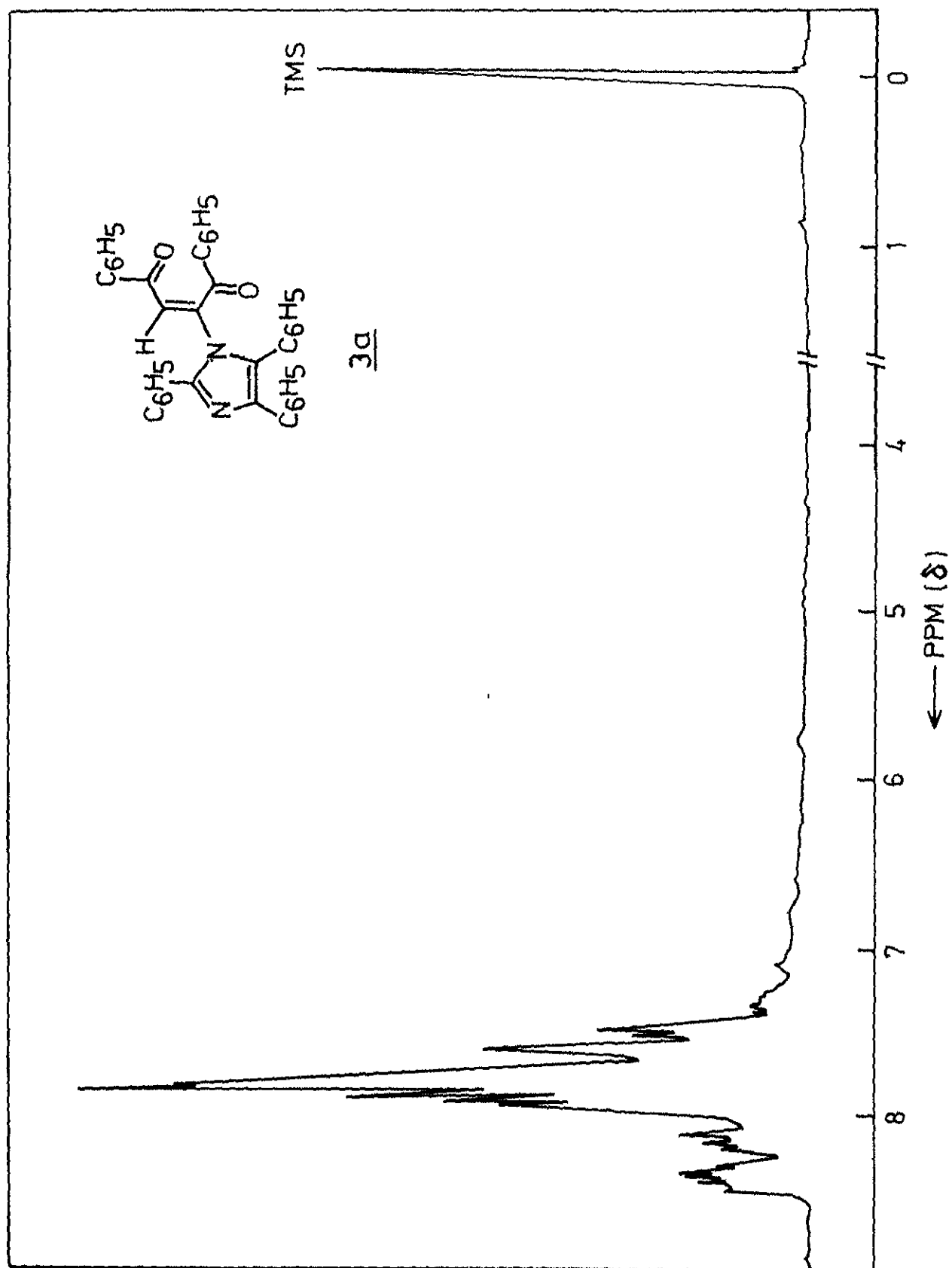
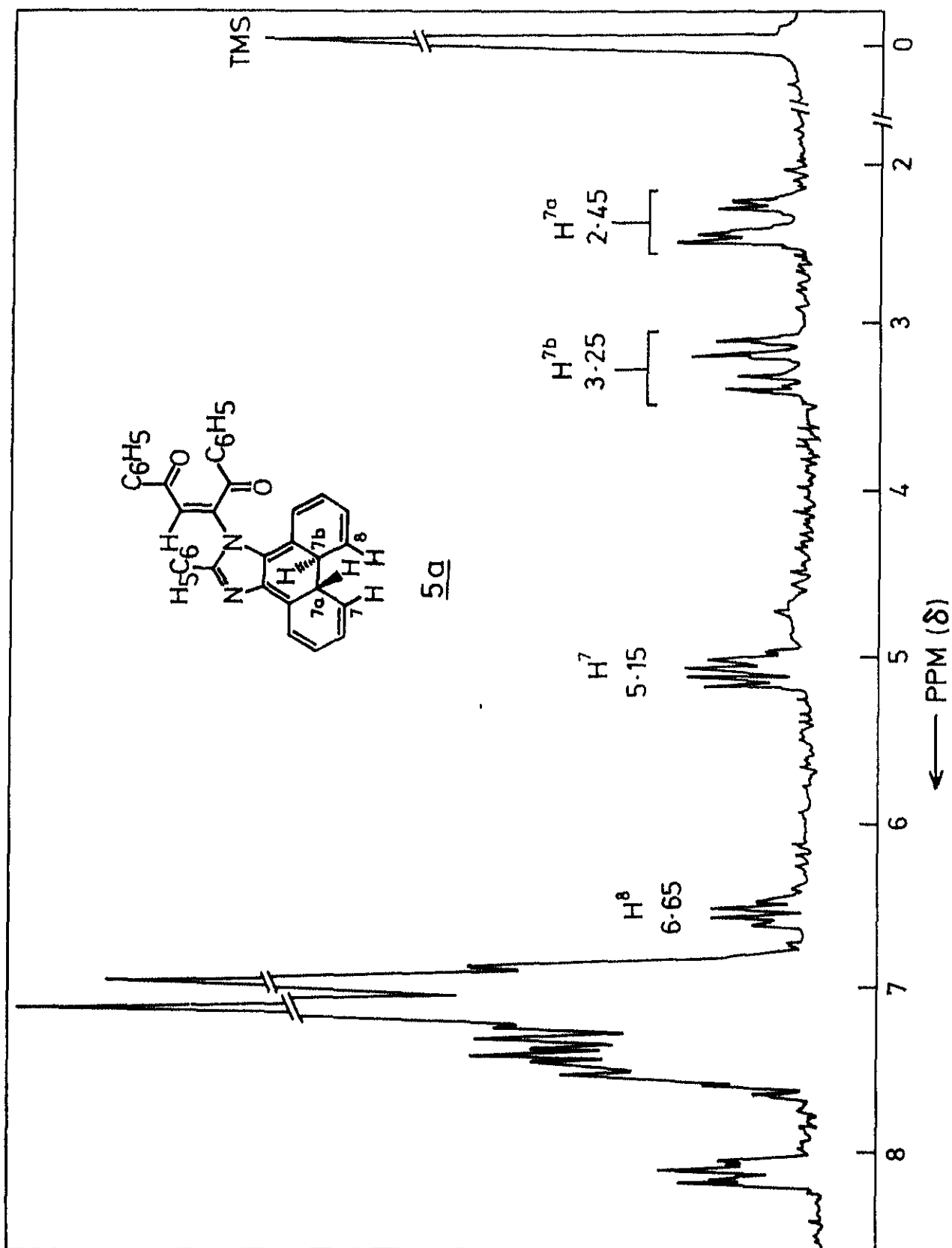


Figure II-1 ^1H NMR spectrum (90 MHz) of 3a.

Figure II-2 ^1H NMR spectrum (90 MHz) of **5a**.

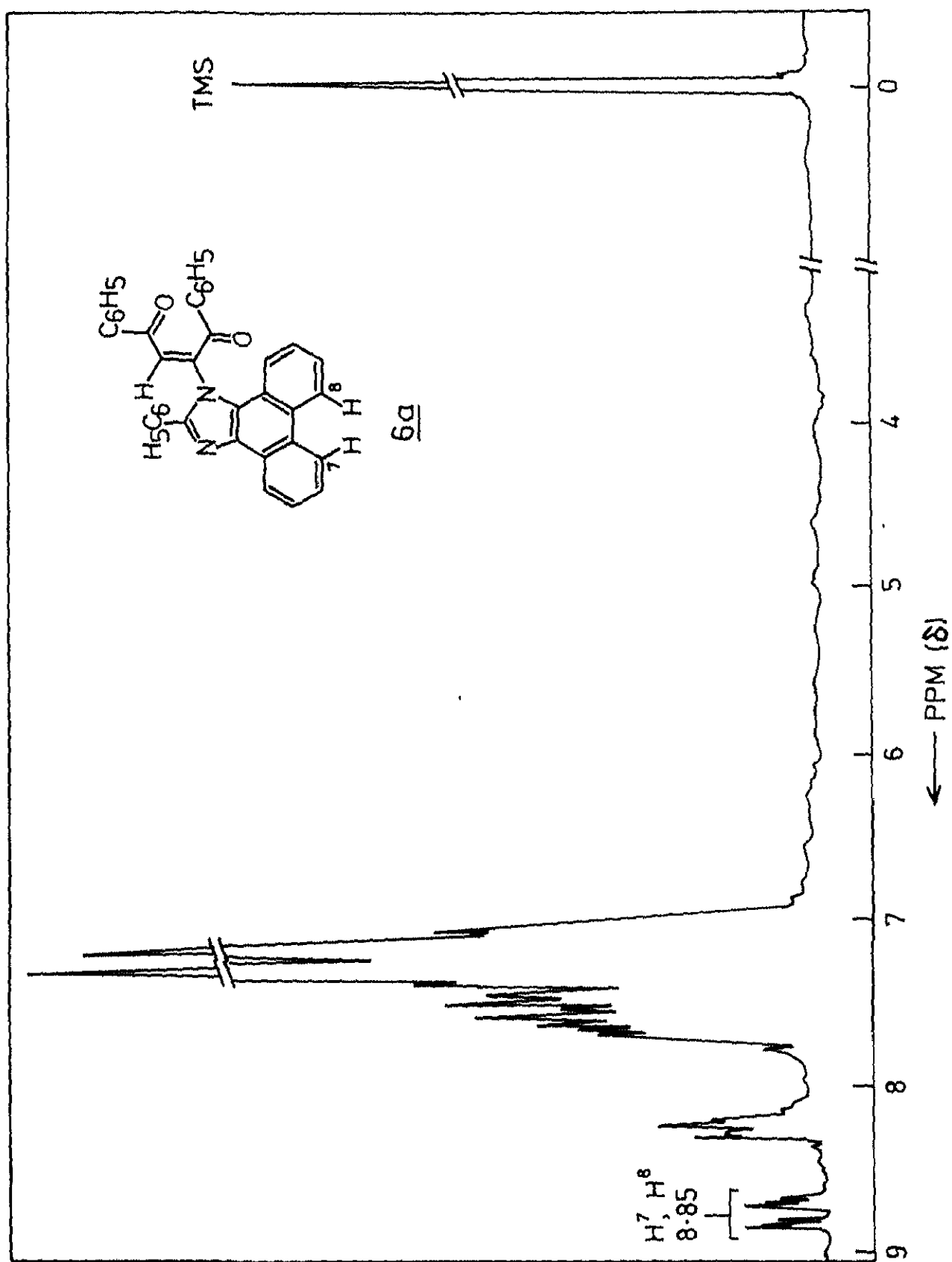


Figure 11-3 ^1H NMR spectrum (90 MHz) of 6a.

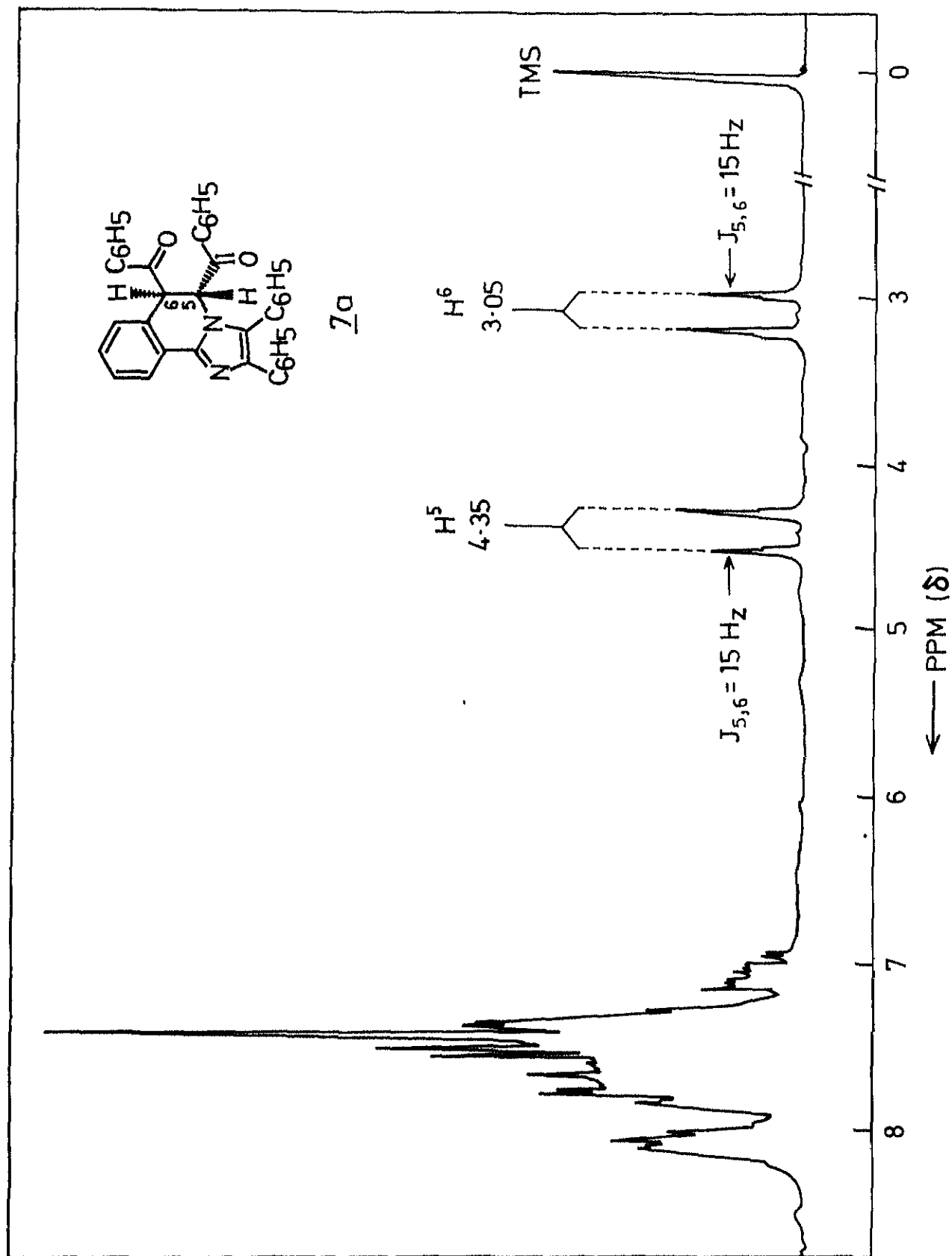


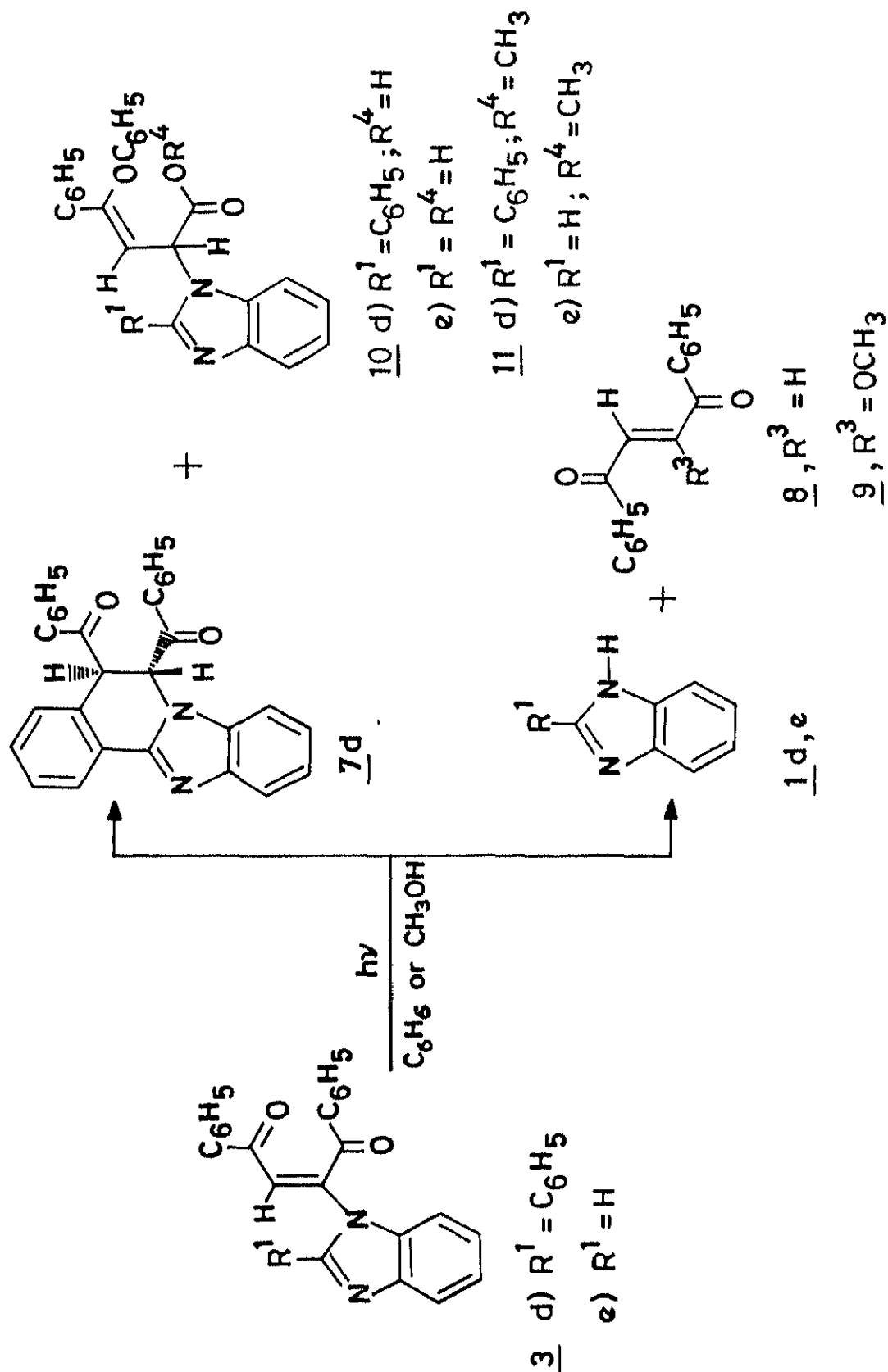
Figure II-4 ^1H NMR spectrum (90 MHz) of **7a**.

1,2-dibenzoyl ethylene (6b, 24%), 4,5-diphenylimidazole (1b, 35%), and trans-1,2-dibenzoyl ethylene (8, 12%), whereas the irradiation of 3b in methanol yielded 16% of 5b, 28% of 6b, 38% of 1a and 17% of 9. Likewise, the irradiation of 3c in benzene gave a 31% yield of threo-5,6-dibenzoyl-2,3-dimethylimidazolo[2,1-a]-5,6-dihydroisoquinoline (7c), a 47% yield of 1c, and a 15% yield of 8, whereas the irradiation of 3c in methanol gave a 25% yield of 7c, a 59% yield of 1c, and a 23% yield of 9.

In contrast, the irradiation of 3d in benzene gave a mixture of threo-5,6-dibenzoylbenzimidazolo[2,1-a]-5,6-dihydroisoquinoline (7d, 13%), 2-(1-(2-phenylbenzimidazolyl))-4-phenoxy-4-phenyl-3-butenic acid (10d, 9%), 2-phenylbenzimidazole (1d, 58%), and trans-1,2-dibenzoyl ethylene (8, 18%), whereas the irradiation of 3d in methanol gave a mixture of methyl 2-(1-(2-phenylbenzimidazolyl))-4-phenoxy-4-phenyl-3-butenate (11d, 14%), 7d (8%), 1d (65%), and 9 (27%).

Similarly, the irradiation of 3e in benzene, under analogous conditions, gave a mixture of 2-(1-benzimidazolyl)-4-phenoxy-4-phenyl-3-butenic acid (10e, 19%), benzimidazole (1e, 56%) and trans-1,2-dibenzoyl ethylene (8, 18%). On the other hand, when the irradiation of 3e was carried out in methanol, a mixture of methyl 2-(1-benzimidazolyl)-4-phenoxy-4-phenyl-3-butenate (11e, 22%), 1e (59%) and 9 (21%) was obtained.

The structures of the butenoic acids 10d and 10e and the methyl butenoates 11d and 11e were established on the basis of



analytical results and spectral data. The ^1H NMR spectrum of 10d, for example, showed a doublet at δ 5.90 (1 H, $J = 8$ Hz, D_2O -exchangeable), assigned to the methine proton and a second doublet at δ 6.45 (1 H, $J = 9$ Hz), assigned to the vinylic proton. The aromatic protons appeared as a multiplet centered around δ 7.55 (19 H), whereas the carboxylic acid proton appeared as a broad singlet at δ 7.85 (1 H, D_2O -exchangeable). The ^1H NMR spectrum of 11d on the other hand, showed a singlet at δ 3.75 (3 H), assigned to the ester methoxy protons and two doublets at δ 5.80 (1 H, $J = 8$ Hz, D_2O -exchangeable) and δ 6.35 (1 H, $J = 8$ Hz), assigned to the methine and vinylic protons, respectively. The aromatic protons of 11d appeared as a multiplet centered around δ 7.58 (19 H) (Figure II.5). Similarly, the ^1H NMR spectral data of 10e and 11e are also in agreement with their structural assignments.

Further confirmation of the structures of the butenoic acids 10d and 10e and the esters 11d and 11e was derived by the conversion of 10d and 10e, through treatment with diazomethane, to 11d (68%) and 11e (72%), respectively.

In order to study the photobehavior of the (*Z*)-1-imidazolyl-1,2-dibenzoylalkenes, we have examined the phototransformation of a representative example, namely, (*Z*)-1-(2-phenylbenzimidazolyl)-1,2-dibenzoylethylene (4d). Irradiation of 4d in benzene gave a 8% yield of 10d, a 20% yield of the *E* isomer, 3d, a 10% recovery of the unchanged starting material 4d, a 36% yield of 1d, and a 14% yield of 8.

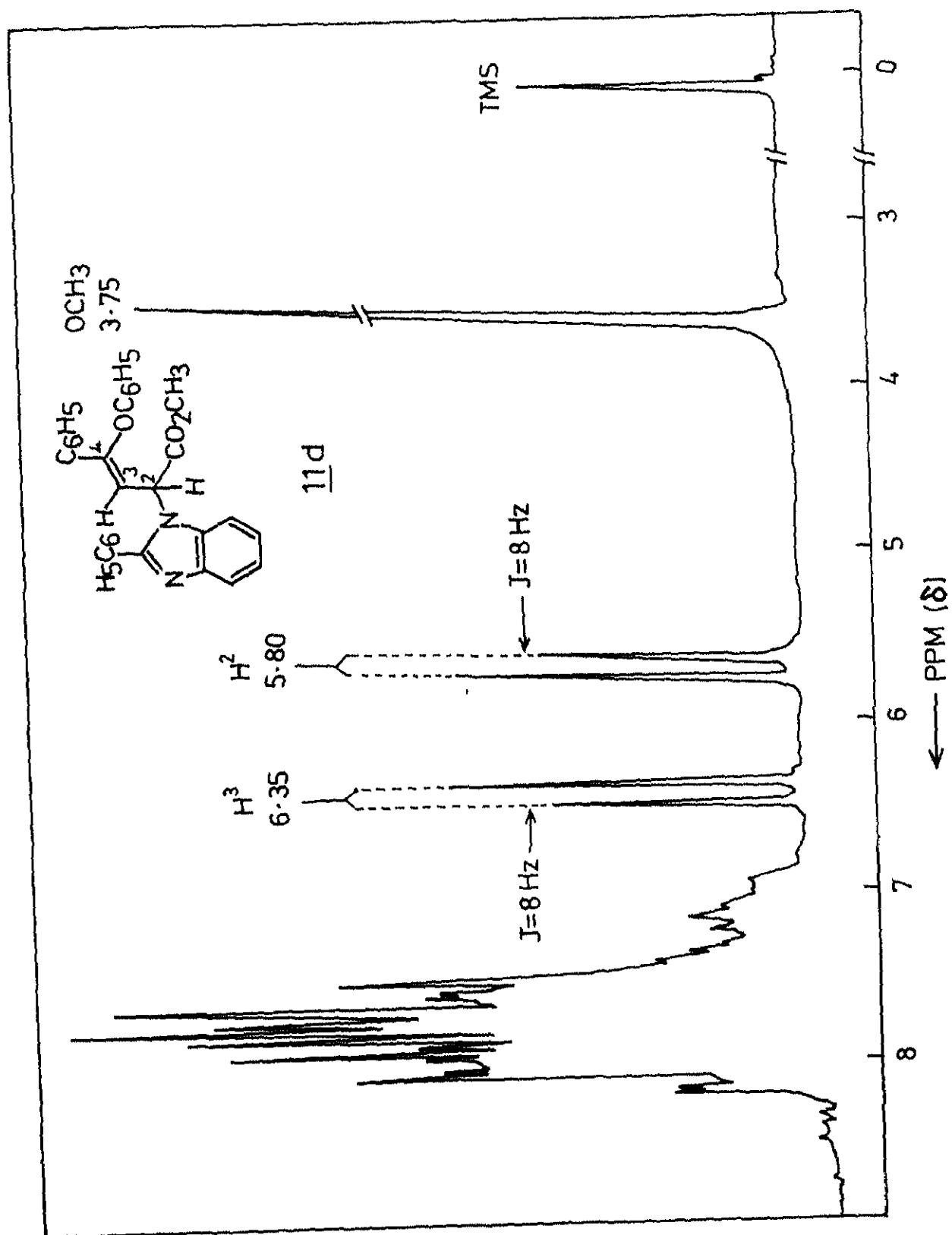
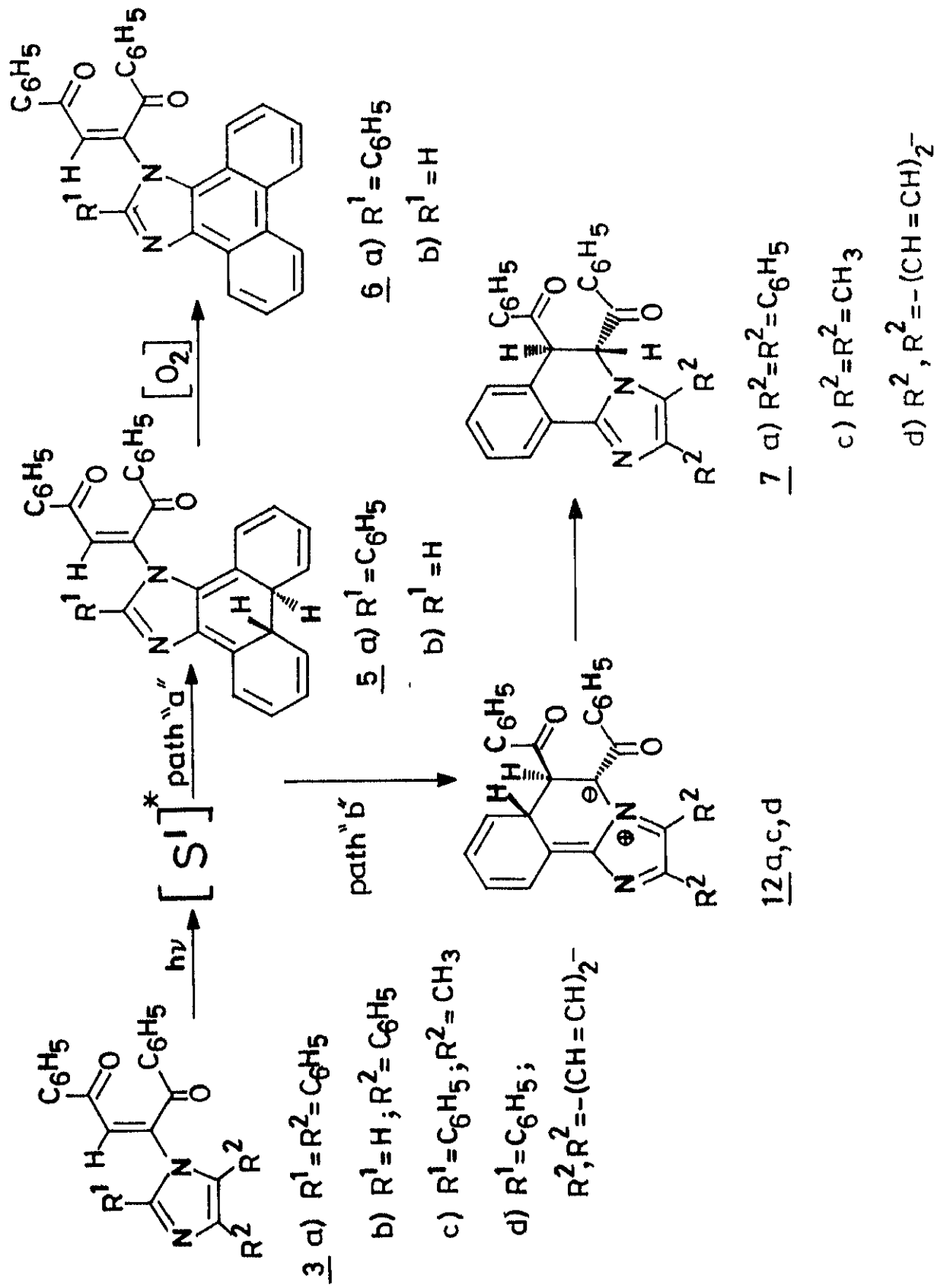


Figure II.5 ^1H NMR spectrum (90 MHz) of **11d**.

II.3.3 Discussion. The formation of the different products in the photoreactions of 1-imidazolyl-1,2-dibenzoylalkenes (3a-e) can be understood in terms of the reaction pathways shown in Schemes II.4-II.6. It is quite evident that the photoreactions of 3a-e are strongly dependent on the substituents present in the imidazolyl component and several pathways, leading to different products are discussed in these cases. One of the photoreactions observed in the case of 3a and 3b, containing phenyl substituents at the C-4 and C-5 positions of the imidazolyl moiety, for example, is a singlet state mediated electrocyclic ring closure reaction, leading to the dihydrophenanthrene derivatives 5a and 5b, respectively (Scheme II.4, path "a"). Such ring closure reactions leading to dihydrophenanthrene derivatives, are well documented in the literature.¹⁸ The formation of the phenanthroimidazolyl-1,2-dibenzoylalkenes 6a and 6b in the photoreactions of 3a and 3b, however, could be understood in terms of the air-oxidation of the dihydrophenanthrene derivatives, 5a and 5b, respectively, under the reaction conditions.

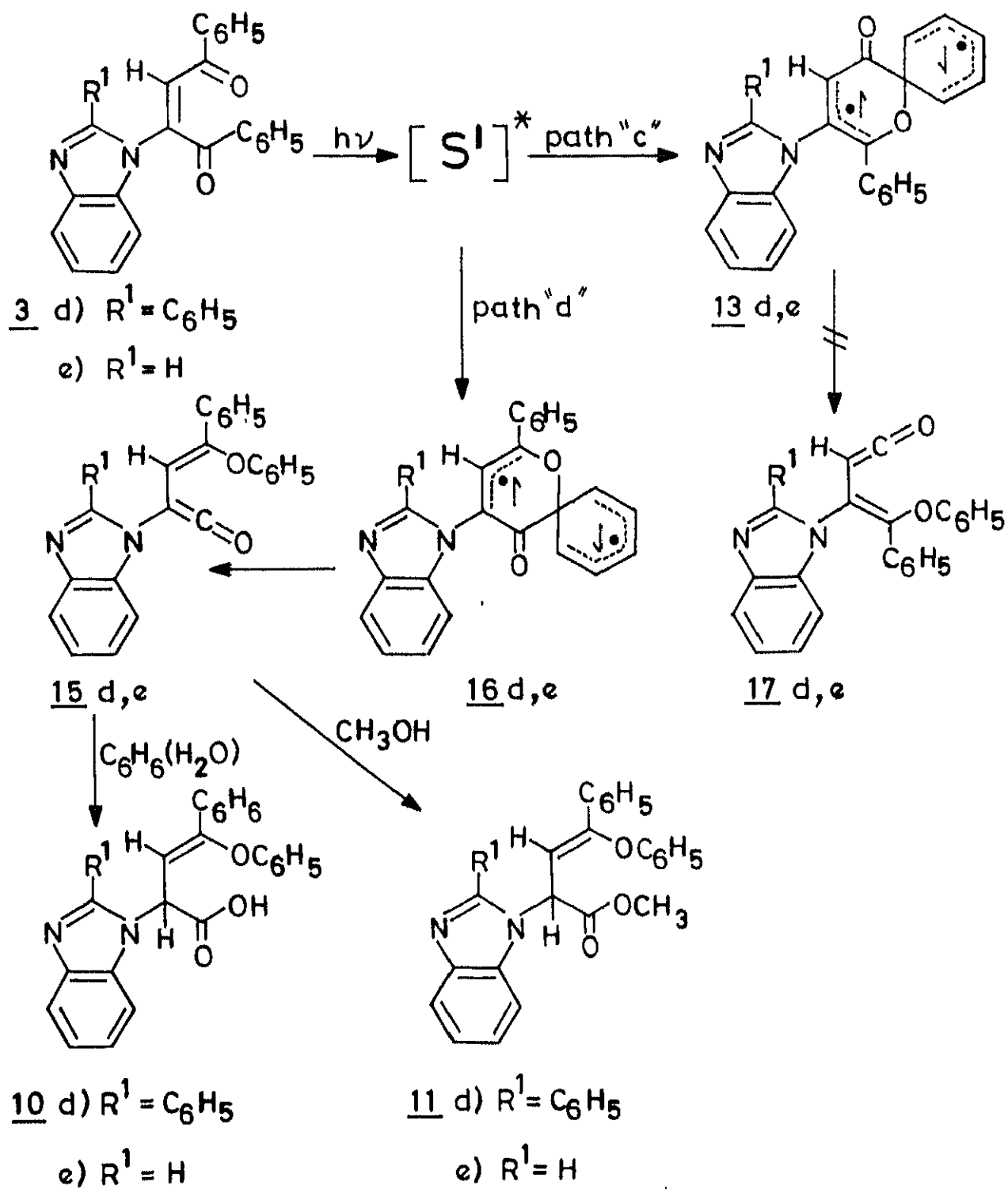
A second mode of reaction, observed in the case of those substrates containing a phenyl substituent in the C-2 position of the imidazolyl component, as in the case of 3a, 3c, and 3d is again a singlet state mediated 10 or 14 electron, electrocyclic, conrotatory ring-closure reaction, involving the phenyl substituent and the 1,2-dibenzoylalkene component, and leading to the zwitterionic intermediates 12a,c,d, as shown in Scheme II.4



(path "b"). Subsequent proton shifts in 12a,c,d through a [1,3] or two successive [1,2] sigmatropic shifts will lead to the imidazolo[2,1-a]-5,6-dihydroisoquinoline derivatives 7a, 7c and 7d, respectively. It may be mentioned here that similar electrocyclic ring-closure reactions have been observed earlier in the photoreactions of 5-phenylsubstituted 1-pyrazolyl-1,2-dibenzoylalkenes, leading to the corresponding pyrazolo[5,1-a]-5,6-dihydroisoquinoline derivatives.¹²

Yet another photoreaction, that has been observed only in the case of 3d and 3e in the present studies, is the 1,2-dibenzoylalkene rearrangement,¹⁻⁶ proceeding through the ketene intermediates 15d,e and leading to the butenoic acids 10d,e or the butenoic esters 11d,e, respectively, depending on the reaction conditions (Scheme II.5, path "d"). On the basis of analogy to the photorearrangements of 1-pyrazolyl-1,2-dibenzoylalkenes,¹² it has been assumed that the ketene intermediates 15d,e are formed from the singlet excited state and involving singlet diradical intermediates 16d,e, as shown in Scheme II.5 (path "d"). It may be pointed out here that the observed regioselectivity, leading to the ketene intermediates 15d,e (Scheme II.5, path "d") as against 17d,e (Scheme II.5, path "e") could be understood in terms of the ground-state conformational preferences of the starting imidazolyl-1,2-dibenzoylalkenes 3d,e. The conformers leading to the diradical intermediates 13d,e (path "c") will be less populated due to steric crowding, as compared to those, leading to the diradical intermediates 16d,e (path "d") and hence the

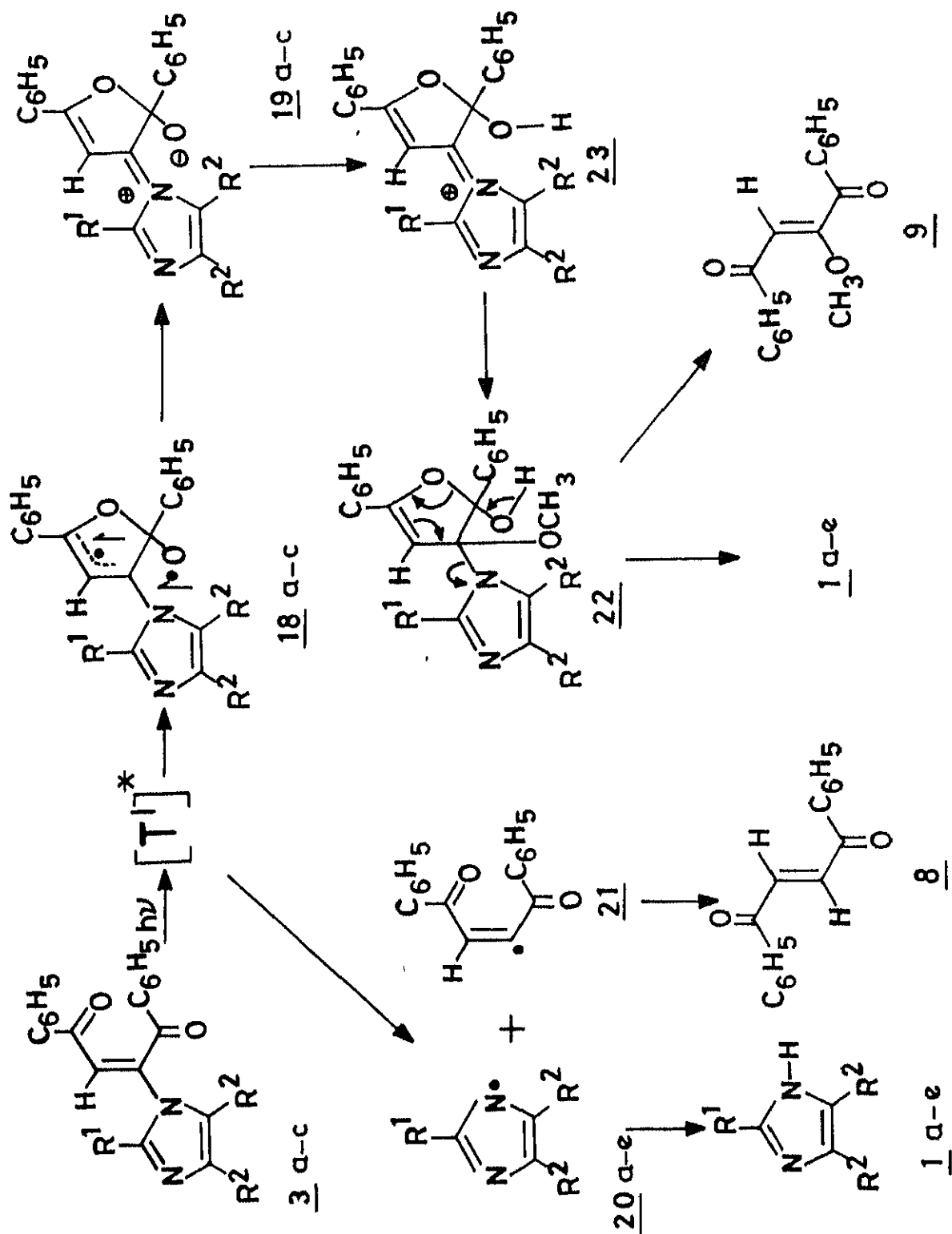
Scheme II.5



observed regioselectivity. It is not very clear why the 1,2-di-benzoylalkene rearrangement has been observed only in the case of 3d and 3e and not in other substrates (3a,b,c), under study. Perhaps, other reactions such as photofragmentations (Scheme II.6) and electrocyclic reactions (Scheme II.4) may be predominant in these cases. Also, steric factors, arising through phenyl or methyl substituents at C-4 and C-5 positions of the imidazolyl moiety, may be adversely affecting the 1,2-dibenzoylalkene rearrangement occurring in 3a,b,c.

The formation of photofragmentation products such as imidazoles (1a-c) or benzimidazoles (1d,e), trans-1,2-dibenzoylethylene (8) and trans-1-methoxy-1,2-dibenzoylethylene (9) in these reactions could be understood in terms of pathways shown in Scheme II.6, involving zwitterionic intermediates (19a-e). A similar pathway has been suggested earlier for the formation of pyrazoles from 1-pyrazolyl-1,2-dibenzoylalkenes.¹² It is also possible that small amounts of 1a-e and 8 in these reactions could arise through radical intermediates such as 20a-e and 21 (Scheme II.6).

II.3.4 Laser Flash Photolysis Studies.¹⁹ Preliminary studies using 337.1 nm laser excitation showed that the flash photolysis of 3a, 3c and 4d in benzene and methanol and of 3d and 3e in benzene led to only very weak, featureless transient absorption phenomena at 350-700 nm in the time domain 0.1-100 μ s. These systems were not pursued in any more detail. In the case



of 3e in benzene ($\lambda_{\text{ex}} = 337.1 \text{ nm}$), ground state bleaching due to photochemical loss was noticed at $\leq 370 \text{ nm}$, suggesting the photoreactive nature of the compound. The laser induced negative absorbance changes did not show any sign of recovery over the longest time scale ($\sim 100 \mu\text{s}$).

The most prominent transient phenomena are observed in the case of 3b. Upon 308 or 337.1 nm laser flash photolysis of 3b in both benzene and methanol, a long-lived transient species with absorption maximum at 640 nm is formed fast within the laser pulse (Figure II.6). As evident from the transient spectrum in benzene (Figure II.6, part A), a second absorption band system is located at 360-390 nm, that this also belongs to the 640 nm species is suggested by the similarity of decay kinetics at the two wavelengths. An important difference noticeable between benzene and methanol (Figure II.6) is that, in the spectral region 350-380 nm, the absorbance change is relatively small in benzene while a growth process leading to pronounced absorbance changes in this region occurs in methanol. The lifetime associated with this growth process is $0.64 \mu\text{s}$.

The presence of oxygen ($\sim 2 \text{ mM}$, air-saturated solutions) does not make any difference to the yields and decay/growth kinetics of the transient absorptions photogenerated from 3b in methanol or benzene. The decay of the 640 nm species becomes enhanced on going from benzene ($\tau = 80 \mu\text{s}$) to methanol ($\tau = 17 \mu\text{s}$). This species is readily quenchable by acids. For example, the unimolecular rate constants for quenching by trifluoroacetic acid

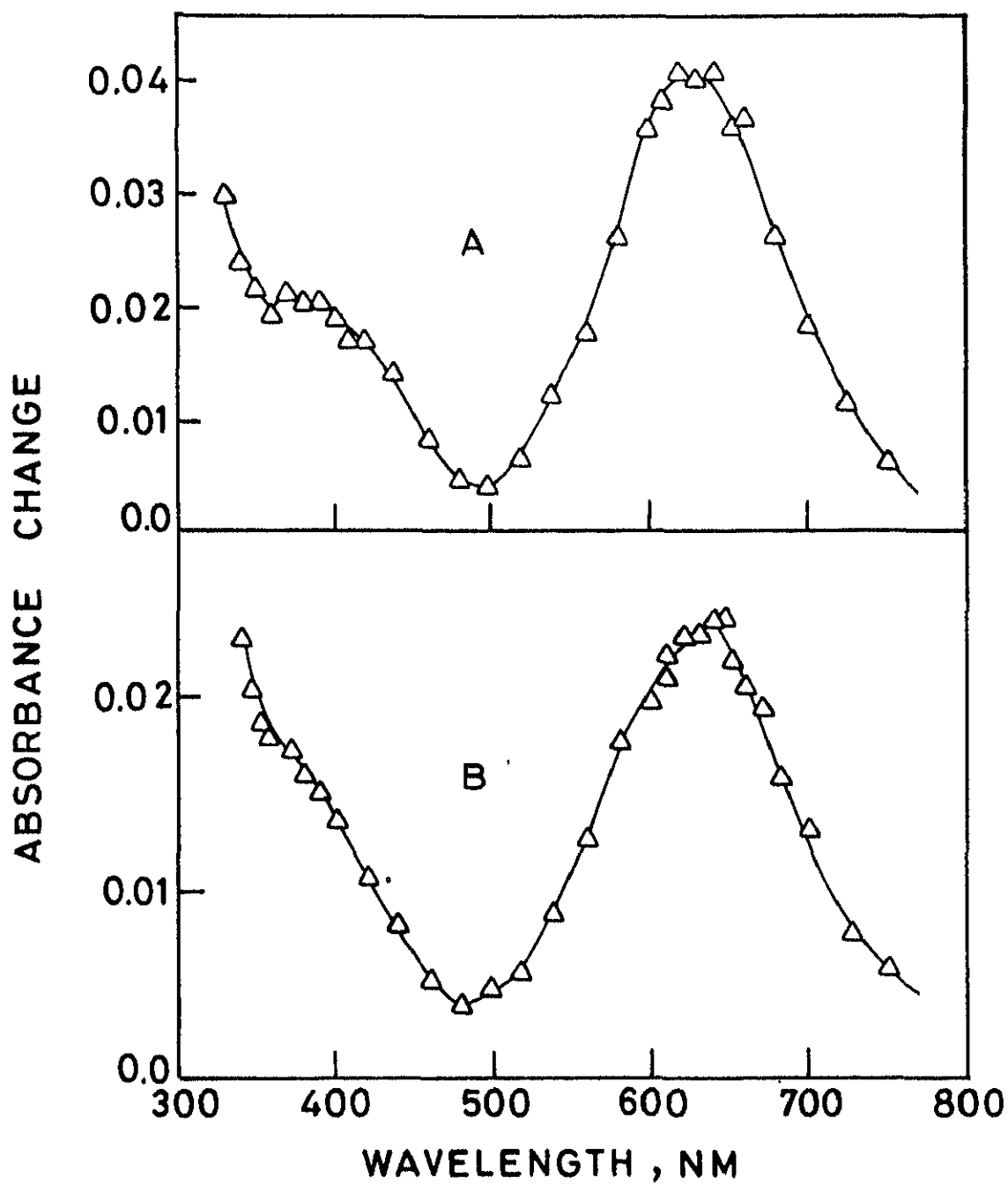


Figure II.6 Transient absorption spectra observed at $2\mu\text{s}$ following 308nm laser flash photolysis of 3b in (A) benzene and (B) methanol.

(in benzene) and hydrochloric acid (in methanol containing 5% H_2O) are 5.0×10^8 and $6.1 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$, respectively. The kinetic data were obtained from the linear dependence of the pseudo first-order rate constant for 640 nm transient absorbance decay on acid concentrations. An alkali, added as tetramethylammonium hydroxide ($\sim 6 \text{ mM}$) in 1:9 $\text{H}_2\text{O}:\text{MeOH}$ (v/v), does not have any noticeable effect on the decay kinetics.

The growth of short-wavelength transient absorption (350-390 nm), observed for 3b in methanol, is found to be common with 3d and 3e in the same solvent (Figure II.7, parts A and B). In particular, the transient processes is very prominent with 3e. It is associated with the reaction of the alcohol with a photo-product, as indicated by the observation of similar, but slower growths of transient absorption in the case of 3e in benzene-methanol mixtures. The transient spectrum in benzene containing 2.5 M methanol is shown in Figure II.7, part C. In aqueous methanol and in the presence of an alkali (tetramethylammonium hydroxide), the methanol-related growth kinetics become enhanced. Table II.1 summarizes the lifetime data associated with the methanol-related processes.

In order to examine if the transient phenomena observed under direct laser excitation are also obtainable under triplet sensitization, experiments were done in which biphenyl triplet was produced by pulse radiolysis.²⁰ In benzene in the presence

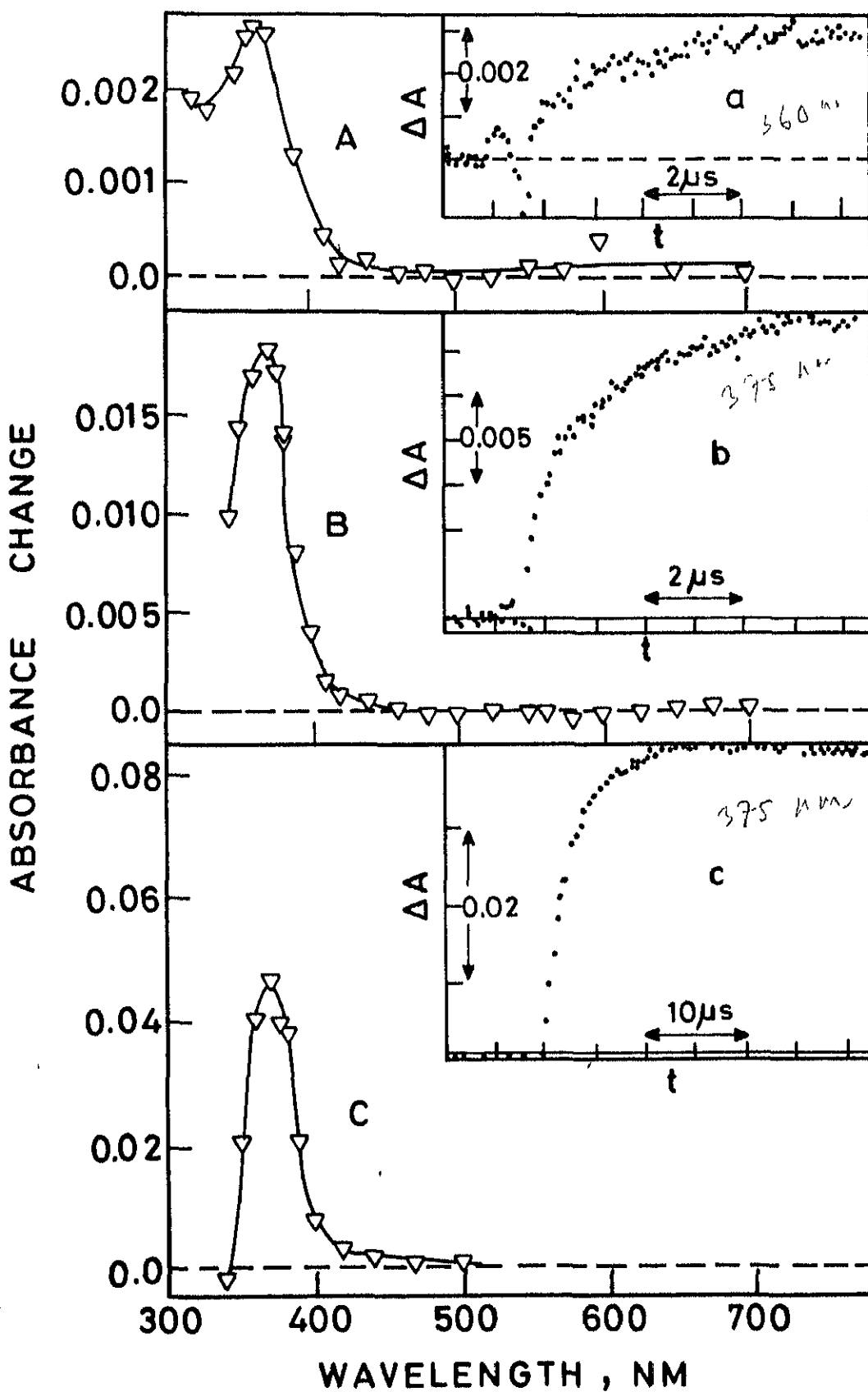


Figure II.7 Transient absorption spectra observed from laser flash photolysis of (A) 3d in methanol ($\lambda_{ex} = 337.1$ nm), (B) 3e in methanol ($\lambda_{ex} = 337.1$ nm) and (C) 3e in benzene + 2.5 M methanol ($\lambda_{ex} = 308$ nm). Insets: Kinetic traces for growth in the respective cases at (a) 360, (b) 375 and (c) 375 nm.

Table II.1. Lifetimes Associated with the Growth Kinetics at 360-390 nm Observed Upon 337.1 or 308 nm Laser Flash Photolysis of 1-Imidazolyl-1,2-dibenzoyl-alkenes in Solvents Containing Methanol.

Substrate	τ , μ s ^a	
	MeOH	MeOH + 5% H ₂ O + 5.6 mM TMAH ^b
<u>3b</u>	0.64	0.26
<u>3d</u>	2.90	0.20
<u>3e</u>	1.90	0.11

a, \pm 15%

b, TMAH = tetramethylammonium hydroxide

of 3b and 3e at 0.5-2.0 mM concentrations. The solutions for these experiments contained 0.05 M biphenyl; at this high concentration, the latter accepted energy from the pulse-radiolytic solvent triplets²⁰ (benzene) and then transferred energy to the substrates. For 3b, concomitant with the decay of biphenyl triplet (monitored at 360 nm), the growth of the 640 nm species has been observed. This is illustrated by the transient spectra and kinetic traces in Figure II.8. This result established that 640 nm species could be produced through the intermediacy of the triplet. In contrast, negative results were obtained concerning the methanol-related growth processes using 3e as the acceptor of energy from biphenyl triplet in benzene + 5-15% methanol. That the biphenyl triplet was pulse-radiolytically produced in the presence of methanol and was quenched by 3e was shown by the enhanced decay of its transient absorption at 360-400 nm. Thus, it is concluded that the photoproduct reacting with methanol in the case of 3e (and by analogy, 3b,d) are singlet-derived. Pulse radiolysis experiments using 3b,c,e at relatively high concentrations (~5 mM) did not furnish evidence for any longlived substrate triplets (with $\tau > 100$ ns). This, coupled with the fact that the formation kinetics of the 640 nm species in the case of 3b matched very well with that of the decay of biphenyl triplet, suggested that the triplets of the dibenzoylalkenes under study are shortlived (< 100 ns).

As discussed in detail in a recent paper¹² on 1-pyrazolyl-1,2-dibenzoylalkenes, the most plausible explanation for the

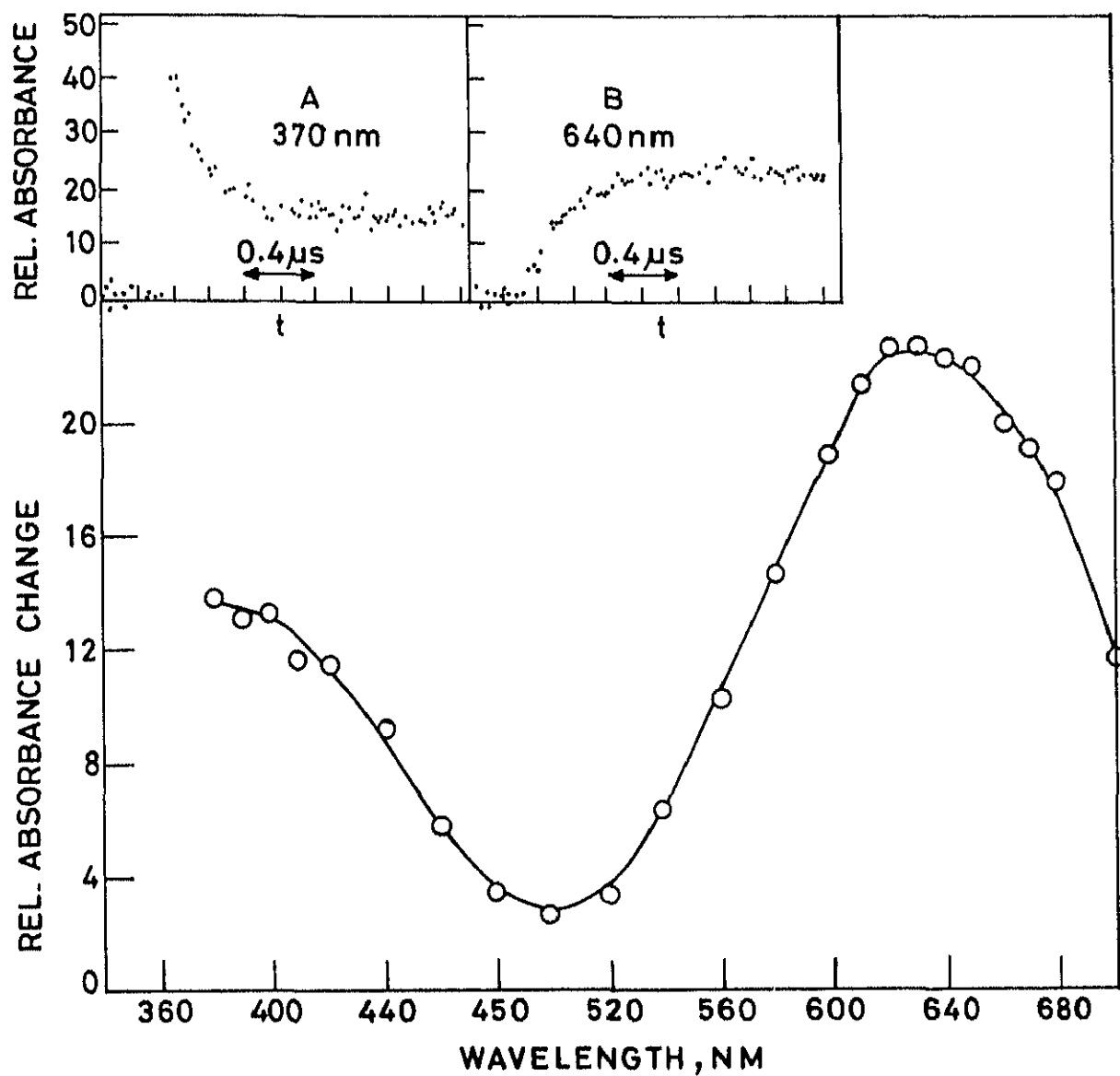
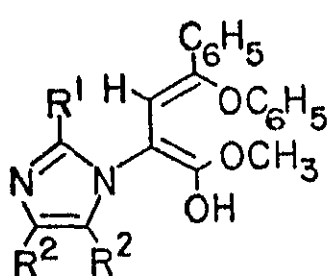
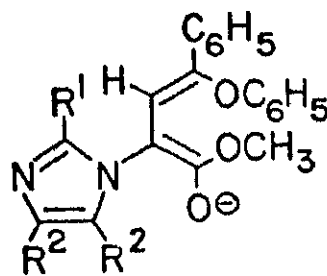


Figure 11.8 Transient absorption spectra at 5 μs following electron pulse irradiation of 0.05M biphenyl in benzene containing 1.1 mM 3b. Insets: kinetic traces showing A decay of biphenyl triplet at 370 nm and B growth of transient absorption at 640 nm.

methanol-related growth phenomena at short wavelengths may be sought in terms of the reaction of the alcohol with the ketene 15 (Scheme II.5), formed as a result of singlet-mediated, intramolecular, phenyl group migration. Thus, the primary species contributing to the plateau absorbance at 350-400 nm following the completion of growth in the presence of methanol can be the enol (24) or the enolate anion (25), depending upon the basicity of the medium. This species undergoes ketonization to the ester on a longer time scale (millisecond). It is to be noted that the



24



25

methanol-related transient phenomena are the most prominent in the case of 3e; this is also the substrate for which the photo-transformation involving intramolecular phenyl group migration occurs with the highest yields (under steady-state irradiation).

The spectral characteristics and quenching behaviors of the 640 nm species from 3b, and its formation via the triplet route are reminiscent of the 600/400 nm species that were commonly observed in the course of the laser flash photolysis of 1-pyrazolyl-1,2-dibenzoylalkenes.¹² In view of its quenching by acids, it appears to be a zwitterion. As reported earlier,¹² a tentative

assignment in terms of the zwitterionic structure 19 has been offered (Scheme II.6); this, however, cannot explain why transient species with similar spectral and kinetic behavior are not observed in the case of 3a,c-e, although the steady-state photo-transformation involving cyclization and methanol addition (Scheme II.6) appears to be pronounced for these substrates also.

II.4 EXPERIMENTAL SECTION

All melting points are uncorrected and were determined on a Mel-Temp melting point apparatus. The IR spectra were recorded on Perkin-Elmer Model 377 or 580 infrared spectrophotometers. The electronic spectra were recorded on Cary 17D or 219 spectrophotometers. ^1H NMR spectra were recorded on either Varian EM-390 or HA-100 NMR spectrometers, whereas ^{13}C NMR spectra were recorded on either Bruker CFT-90 or Varian CFT-20C NMR spectrometers, using tetramethylsilane as internal standard. The mass spectra were recorded on a Varian Mat CH7 or Hitachi RMU-6E single-focussing mass spectrometer at 70 eV. All steady-state irradiations were carried out using Hanovia 450 W medium pressure mercury lamp in a quartz-jacketted immersion well.

II.4.1 Starting Materials. 2,4,5-Triphenylimidazole (1a),^{21,22} mp 271-273 °C, 4,5-diphenylimidazole (1b),²³ mp 231-232 °C, 4,5-dimethyl-2-phenylimidazole (1c),²⁴ mp 142-143 °C, 2-phenylbenzimidazole (1d),²⁵ mp 289-290 °C, benzimidazole

(1e), ²⁶ mp 171 °C and DBA (2), ^{27,28} mp 110-111 °C were prepared by reported procedures. Solvents for steady-state photolysis were purified and distilled before use, whereas Aldrich Gold label solvents were used for laser studies.

II.4.2 Preparation of (E)- and (Z)-1-Imidazolyl-1,2-di-benzoylethylenes 3a-e and 4a-e. A general procedure for the preparation of 3a-e and 4a-e was to reflux a mixture of the appropriate imidazole (1a-c) or benzimidazole (1d,e) (0.01 mol) and DBA (0.01 mol) in acetonitrile for varying periods of time. Removal of the solvent under vacuum gave a residual solid, which was chromatographed on silica gel and eluted with a mixture of benzene and petroleum ether to give the Z isomer first, followed by the E isomer. These adducts were purified, in each case, by recrystallization from suitable solvents.

(Z)-1-(2,4,5-Triphenylimidazolyl)-1,2-dibenzoylethylene (4a). 4a was obtained in a 22% yield (elution with a 1:3 mixture of benzene and petroleum ether and recrystallization from a 1:1 mixture of benzene and petroleum ether), mp 194-195 °C.

IR spectrum ν_{\max} (KBr): 3060 and 3040 (ν_{CH}), 1675 and 1660 ($\nu_{\text{C=O}}$), and 1600 ($\nu_{\text{C=C}}$) cm^{-1} .

UV spectrum λ_{\max} (methanol): 220 nm (ϵ , 54,750), and 278 (53,000).

¹H NMR spectrum (CDCl_3): δ 7.10-8.20 (m, vinylic and aromatic).

Mass spectrum, m/e (relative intensity): 530 (M^+ , 94), 453 ($M^+ - C_6H_5$, 9), 425 ($M^+ - COC_6H_5$, 23), 424 (58), 348 (37), 320 (3), 295 (53), 105 ($C_6H_5CO^+$, 100), and 77 ($C_6H_5^+$, 73).

Anal. Calcd for $C_{37}H_{26}N_2O_2$: C, 83.77; H, 4.91; N, 5.28.
Found: C, 84.05; H, 4.70; N, 5.51.

(E)-1-(2,4,5-Triphenylimidazolyl)-1,2-dibenzoylethylene (3a). 3a was obtained in a 66% yield (elution with a 1:2 mixture of benzene and petroleum ether and recrystallization from a 1:1 mixture of benzene and petroleum ether), mp 175 °C.

IR spectrum ν_{max} (KBr): 3065 and 3045 (ν_{CH}), 1675 and 1660 ($\nu_{C=O}$), and 1605 ($\nu_{C=C}$) cm^{-1} .

UV spectrum λ_{max} (methanol): 223 nm (ϵ , 47,350), and 270 (46,100).

Mass spectrum, m/e (relative intensity): 530 (M^+ , 93), 453 ($M^+ - C_6H_5$, 8), 425 ($M^+ - COC_6H_5$, 25), 424 (46), 348 (38), 320 (3), 295 (55), 105 ($C_6H_5CO^+$, 100), and 77 ($C_6H_5^+$, 74).

Anal. Calcd for $C_{37}H_{26}N_2O_2$: C, 83.77; H, 4.91; N, 5.28.
Found: C, 83.45; H, 4.63; N, 5.41.

(Z)-1-(4,5-diphenylimidazolyl)-1,2-dibenzoylethylene (4b). 4b was obtained in a 11% yield (elution with a mixture (1:3) of benzene and petroleum ether and recrystallization from a 1:1 mixture of benzene and petroleum ether), mp 153 °C.

IR spectrum ν_{max} (KBr): 3080, 3060 and 3035 (ν_{CH}), 1675 1660 ($\nu_{C=O}$), 1617 and 1595 ($\nu_{C=C}$) cm^{-1} .

UV spectrum λ_{\max} (methanol): 228 nm (ϵ , 37,600), and 270 (40,300).

^1H NMR spectrum (CDCl_3): δ 7.00-8.35 (m, vinylic and aromatic).

Mass spectrum, m/e (relative intensity): 454 (M^+ , 73), 377 ($\text{M}^+ - \text{C}_6\text{H}_5$, 5), 349 ($\text{M}^+ - \text{COC}_6\text{H}_5$, 33), 248 (46), 272 (54), 219 (17), 105 ($\text{C}_6\text{H}_5\text{CO}^+$, 100), and 77 (C_6H_5 , 79).

Anal. Calcd for $\text{C}_{31}\text{H}_{22}\text{N}_2\text{O}_2$: C, 81.94; H, 4.85; N, 6.17.
Found: C, 81.63; H, 4.55; N, 6.39.

(E)-1-(4,5-Diphenylimidazolyl)-1,2-dibenzoyl ethylene (3b).

3b was obtained in a 74% yield (elution with a 1:2 mixture of benzene and petroleum ether and recrystallization from a 1:1 mixture of benzene and petroleum ether), mp 175 °C.

IR spectrum ν_{\max} (KBr): 3080, 3065 and 3036 (ν_{CH}), 1675 and 1660 ($\nu_{\text{C=O}}$), 1612 and 1595 ($\nu_{\text{C=C}}$) cm^{-1} .

UV spectrum λ_{\max} (methanol): 225 nm (ϵ , 35,970), and 261 (38,070).

^1H NMR spectrum (CDCl_3): δ 7.05-8.30 (m, vinylic and aromatic).

Mass spectrum, m/e (relative intensity): 454 (M^+ , 73), 377 ($\text{M}^+ - \text{C}_6\text{H}_5$, 4), 349 ($\text{M}^+ - \text{COC}_6\text{H}_5$, 36), 348 (43), 272 (57), 219 (28), 105 ($\text{C}_6\text{H}_5\text{CO}^+$, 100), and 77 (C_6H_5^+ , 78).

Anal. Calcd for $\text{C}_{31}\text{H}_{22}\text{N}_2\text{O}_2$: C, 81.94; H, 4.85; N, 6.17.
Found: C, 82.15; H, 5.05; N, 6.32.

(Z)-1-(4,5-Dimethyl-2-phenylimidazolyl)-1,2-dibenzoyl-ethylene (4c). 4c was obtained in a 4% yield (elution with a 1:2 mixture of benzene and petroleum ether and recrystallization from a 1:1 mixture of methylene chloride and petroleum ether), mp 188 °C.

IR spectrum ν_{\max} (KBr): 3090, 3065, 3045, 2975 and 2875 (ν_{CH}), 1670 and 1660 ($\nu_{\text{C=O}}$), and 1610 ($\nu_{\text{C=C}}$).

UV spectrum λ_{\max} (methanol): 218 nm (ϵ , 27,350), and 272 (46,130).

^1H NMR spectrum (CDCl_3): δ 1.95 (s, 3 H, CH_3), 2.45 (s, 3 H, CH_3), and 7.05-8.35 (m, 16 H, vinylic and aromatic).

Anal. Calcd for $\text{C}_{27}\text{H}_{22}\text{N}_2\text{O}_2$: C, 79.80; H, 5.42; N, 6.90. Found: C, 80.11; H, 5.68; 7.15.

(E)-1-(4,5-Dimethyl-2-phenylimidazolyl)-1,2-dibenzoyl-ethylene (3c). 3c was obtained in a 74% yield (elution with a 1:1 mixture of benzene and petroleum ether and recrystallization from a 1:1 mixture of methylene chloride and petroleum ether), mp 173-174 °C.

IR spectrum ν_{\max} (KBr): 3085, 3065, 3040, 2975 and 2880 (ν_{CH}), 1670 and 1660 ($\nu_{\text{C=O}}$), and 1608 ($\nu_{\text{C=C}}$) cm^{-1} .

UV spectrum λ_{\max} (methanol): 215 nm (ϵ , 22,960), and 263 (44,240).

^1H NMR spectrum (CDCl_3): δ 1.85 (s, 3 H, CH_3), 2.35 (s, 3 H, CH_3), and 7.05-8.20 (m, 16 H, vinylic and aromatic).

Mass spectrum, m/e (relative intensity): 406 (M^+ , 83), 329 ($M^+ - C_6H_5$, 5), 301 ($M^+ - COC_6H_5$, 23), 300 (36), 224 ($M^+ - COC_6H_5$, $-C_6H_5$, 38), 170 (11), 105 ($C_6H_5CO^+$, 100), and 77 (C_6H_5 , 75).

Anal. Calcd for $C_{27}H_{22}N_2O_2$: C, 79.80; H, 5.42; N, 6.90.
Found: C, 79.55; H, 5.28; N, 7.19.

(Z)-1-(2-Phenylbenzimidazolyl)-1,2-dibenzoyl ethylene (4d)
4d was obtained in a 35% yield (elution with a 1:4 mixture of benzene and petroleum ether and recrystallization from a 1:1 mixture of benzene and petroleum ether), mp 170 °C.

IR spectrum ν_{max} (KBr): 3090, 3060, and 3035 (ν_{CH}), 1660 and 1650 ($\nu_{C=O}$), and 1605 ($\nu_{C=C}$) cm^{-1} .

UV spectrum λ_{max} (methanol): 219 nm (ϵ , 37,830), 239 (31,480), and 280 (35,900).

1H NMR spectrum ($CDCl_3$): δ 6.90-8.30 (m, vinylic and aromatic).

Mass spectrum, m/e (relative intensity): 428 (M^+ , 98), 351 ($M^+ - C_6H_5$, 7), 323 ($M^+ - COC_6H_5$, 31), 322 (49), 246 (21), 218 ($M^+ - 2CO_6H_5$, 3), 193 (9), 105 ($C_6H_5CO^+$, 100), and 77 ($C_6H_5^+$, 76).

Anal. Calcd for $C_{29}H_{20}N_2O_2$: C, 81.31; H, 4.67; N, 6.54.
Found: C, 81.56; H, 4.71; N, 6.38.

(E)-1-(2-Phenylbenzimidazolyl)-1,2-dibenzoyl ethylene (3d).
3d was obtained in a 58% yield (elution with a 1:2 mixture of

benzene and petroleum ether and recrystallization from a 1:1 mixture of benzene and petroleum ether), mp 197-198 °C.

IR spectrum ν_{\max} (KBr): 3085, 3065 and 3040 (ν_{CH}), 1665 and 1655 ($\nu_{\text{C=O}}$), and 1610 ($\nu_{\text{C=C}}$) cm^{-1} .

UV spectrum λ_{\max} (methanol): 220 nm (ϵ , 35,100), 237 (31,030), and 271 (32,740).

^1H NMR spectrum (CDCl_3): δ 6.90-8.60 (m, vinylic and aromatic).

Mass spectrum, m/e (relative intensity): 428 (M^+ , 96), 351 ($\text{M}^+ - \text{C}_6\text{H}_5$, 8), 323 ($\text{M}^+ - \text{COC}_6\text{H}_5$, 33), 322 (50), 246 (21), 218 (3), 193 (9), 105 ($\text{C}_6\text{H}_5\text{CO}^+$, 100), and 77 (C_6H_5^+ , 79).

Anal. Calcd for $\text{C}_{29}\text{H}_{20}\text{N}_2\text{O}_2$: C, 81.31; H, 4.67; N, 6.54. Found: C, 81.60; H, 4.38; N, 6.33.

(Z)-1-(Benzimidazolyl)-1,2-dibenzoylethylene (4e). 4e was obtained in a 6% yield (elution with a 1:4 mixture of benzene and petroleum ether and recrystallization from a 1:1 (mixture of benzene and petroleum ether), mp 161-162 °C.

IR spectrum ν_{\max} (KBr): 3085 and 3065 (ν_{CH}), 1665 and 1655 ($\nu_{\text{C=O}}$), and 1615 ($\nu_{\text{C=C}}$) cm^{-1} .

UV spectrum λ_{\max} (methanol): 220 nm (ϵ , 24,120), 260 (29,800), and 323 (8,800).

^1H NMR spectrum (CDCl_3): δ 7.00-8.60 (m, vinylic and aromatic protons).

Anal. Calcd for $C_{23}H_{16}N_2O_2$: C, 78.41; H, 4.55; N, 7.95.
Found: C, 78.66; H, 4.81; N, 8.17.

(E)-1-Benzimidazolyl-1,2-dibenzoylethylene (3e). 3e was obtained in a 82% yield (elution with a 1:2 mixture of benzene and petroleum ether and recrystallization from a 1:1 mixture of benzene and petroleum ether, mp 146 °C.

IR spectrum ν_{\max} (KBr): 3080 and 3065 (ν_{CH}), 1665 and 1655 ($\nu_{C=O}$), and 1610 ($\nu_{C=C}$) cm^{-1} .

UV spectrum λ_{\max} (methanol): 218 nm (ϵ , 22,180), 251 (27,820), and 314 (8,130).

1H NMR spectrum ($CDCl_3$): δ 6.90-8.55 (m, aromatic and vinylic).

Mass spectrum, m/e (relative intensity): 352 (M^+ , 100), 275 ($M^+ - C_6H_5$, 6), 247 ($M^+ - COC_6H_5$, 19), 246 (53), 170 ($M^+ - COC_6H_5 - C_6H_5$, 23), 117 (71), 105 ($C_6H_5CO^+$, 98), and 77 (75).

Anal. Calcd for $C_{23}H_{16}N_2O_2$: C, 78.41; H, 4.55; N, 7.95.
Found: C, 78.42; H, 4.80; N, 7.68.

II.4.3 Irradiation of (E)-1-(2,4,5-Triphenylimidazolyl)-1,2-dibenzoylethylene. A In Benzene. A benzene solution of 3a (500 mg, 0.943 mmol, in 500 mL) was purged with nitrogen and irradiated for 1.5 h. Removal of the solvent under reduced pressure gave a residual solid which was chromatographed over silica gel. Elution with petroleum ether gave 15 mg (6%) of trans-dibenzoylethylene (8), mp 109 °C (mixture melting point),

after recrystallization from methanol.

Subsequent elution of the column with a mixture (1:4) of benzene and petroleum ether gave 90 mg (18%) of threo-5,6-di-benzoyl-2,3-diphenylimidazolo[2,1-a]-5,6-dihydroisoquinoline (7a), mp 218-219 °C, after recrystallization from a mixture (1:1) of benzene and petroleum ether.

IR spectrum ν_{\max} (KBr): 3075, 3035, 2960 and 2898 (ν_{CH}), 1682 and 1675 ($\nu_{\text{C=O}}$) and 1590 ($\nu_{\text{C=C}}$) cm^{-1} .

UV spectrum λ_{\max} (methanol): 220 nm (ϵ , 45,350) and 249 (14,800).

^{13}C NMR spectrum (CDCl_3): δ 50.13 (C-6), 62.81 (C-5), 118.21, 120.73, 121.22, 122.35, 122.73, 122.99, 123.12, 123.61, 125.37, 125.49, 125.84, 126.23, 126.34, 127.54, 127.67, 127.71, 128.83, 128.91, 129.15, 129.37, 130.74, 142.33, 148.75, 155.77, 192.30 (C=O), and 193.47 (C=O).

Mass spectrum, m/e (relative intensity): 530 (M^+ , 3), 453 ($\text{M}^+ - \text{C}_6\text{H}_5$, 7), 425 ($\text{M}^+ - \text{COC}_6\text{H}_5$, 53), 424 ($\text{M}^+ - \text{COC}_6\text{H}_5 - \text{H}$, 55), 320 ($\text{M}^+ - 2\text{COC}_6\text{H}_5$, 31), 294 (7), and 105 ($\text{C}_6\text{H}_5\text{CO}^+$, 100).

Anal. Calcd for $\text{C}_{37}\text{H}_{26}\text{N}_2\text{O}_2$: C, 83.77; H, 3.91; N, 5.28. Found: C, 84.08; H, 4.74; N, 5.45.

Further elution of the column with a mixture (1:1) of benzene and petroleum ether gave 110 mg (22%) of 5a, mp 227-228 °C, after recrystallization from a mixture (1:1) of methylene chloride and petroleum ether.

IR spectrum ν_{\max} (KBr): 3078, 3035, 2975 and 2895 (ν_{CH}), 1665 and 1655 ($\nu_{\text{C=O}}$), 1600 and 1590 ($\nu_{\text{C=C}}$) cm^{-1} .

UV spectrum λ_{\max} (methanol): 236 nm (ϵ , 29,800), 290 (16,130), and 314 (19,150).

Mass spectrum, m/e (relative intensity): 530 (M^+ , 3), 528 ($\text{M}^+ - 2\text{H}$, 100), 453 ($\text{M}^+ - \text{C}_6\text{H}_5$, 9), 451 ($\text{M}^+ - \text{C}_6\text{H}_5$, -2H , 41), 425 ($\text{M}^+ - \text{COC}_6\text{H}_5$, 4), 423 ($\text{M}^+ - \text{COC}_6\text{H}_5$, -2H , 38), 422 (45), 320 ($\text{M}^+ - 2\text{COC}_6\text{H}_5$, 4), 318 (12), 293 ($\text{C}_{21}\text{H}_{13}\text{N}_2^+$, 53), 216 (10), and 105 ($\text{C}_6\text{H}_5\text{CO}^+$, 89).

Anal. Calcd for $\text{C}_{37}\text{H}_{26}\text{N}_2\text{O}_2$: C, 83.77; H, 4.91; N, 5.28.
Found: C, 83.49; H, 4.63; N, 5.47.

Subsequent elution of the column with a mixture (4:1) of benzene and petroleum ether gave 100 mg (20%) of 6a, mp 258-259 $^{\circ}\text{C}$, after recrystallization from a mixture (1:1) of methylene chloride and petroleum ether.

IR spectrum ν_{\max} (KBr): 3075 and 3035 (ν_{CH}), 1670 and 1660 ($\nu_{\text{C=O}}$), 1610 and 1590 ($\nu_{\text{C=C}}$) cm^{-1} .

UV spectrum λ_{\max} (methanol): 223 nm (ϵ , 30,990), and 254 (54,790).

^{13}C NMR spectrum (CDCl_3): δ 114.34, 115.21, 118.15, 118.99, 119.21, 119.67, 120.37, 120.63, 123.25, 123.68, 124.12, 124.26, 124.64, 124.85, 125.27, 126.18, 126.38, 132.33, 132.98, 133.46, 134.55, 142.18, 143.17, 154.53, 156.78, 158.35, 193.20 (C=O), and 194.18 (C=O).

Mass spectrum, m/e (relative intensity): 528 (M^+ , 100), 451 ($M^+ - C_6H_5$, 37), 423 ($M^+ - COC_6H_5$, 33), 422 (44), 346 (3), 318 (11), 293 (55), 216 (11), 105 ($C_6H_5CO^+$, 91).

Anal. Calcd for $C_{37}H_{24}N_2O_2$: C, 84.09; H, 4.55; N, 5.30.
Found: C, 84.23; H, 4.41; N, 5.51.

The column was finally eluted with benzene to give 50 mg (17%) of 2,4,5-triphenylimidazole (1a), mp 271-272 °C (mixture melting point), after recrystallization from 50% acetic acid.

B In Air-Saturated Benzene. A solution of 3a in benzene (500 mg, 0.943 mmol in 500 mL) was saturated with air and irradiated for 1.5 h. Workup as in the earlier case by removal of the solvent under vacuum and chromatographing the residue over silica gel gave 25 mg (11%) of 8 (elution with petroleum ether), mp 109 °C (mixture melting point) 50 mg (10%) of 7a (elution with a 1:4 mixture of benzene and petroleum ether and recrystallization from a 1:1 mixture of benzene and petroleum ether, mp 217-218 °C (mixture melting point), 150 mg (31%) of 6a (elution with benzene and recrystallization from a 1:1 mixture of methylene chloride and petroleum ether), mp 258-259 °C (mixture melting point) and 100 mg (34%) of 1a (elution with a 9:1 mixture of benzene and ethyl acetate and recrystallization from 50% acetic acid), mp 271-272 °C (mixture melting point).

C In Methanol. A methanol solution of 3a (500 mg, 0.943 mmol in 500 mL) was irradiated for 1.5 h and worked up as in the

earlier cases to give 35 mg (14%) of trans-2-methoxy-1,2-dibenzoylethylene (9) (elution with petroleum ether and recrystallization from methanol), mp 108 °C (mixture melting point), 50 mg (10%) of 7a (elution with a 1:4 mixture of benzene and petroleum ether and recrystallization from a 1:1 mixture of benzene and petroleum ether), mp 217-218 °C (mixture melting point), 75 mg (15%) of 5a (elution with a 1:1 mixture of benzene and petroleum ether and recrystallization from a 1:1 mixture of methylene chloride and petroleum ether), mp 227-228 °C (mixture melting point), 120 mg (25%) of 6a (elution of 4:1 mixture of benzene and petroleum ether and recrystallization from a 1:1 mixture of methylene chloride and petroleum ether) and 100 mg (34%) of 1a (elution with a 9:1 mixture of benzene and ethyl acetate and recrystallization from 50% acetic acid), mp 271-272 °C (mixture melting point).

II.4.4 Air-Oxidation of 5a to 6a. A solution of 5a (50 mg, 0.094 mmol) in benzene (40 mL) was refluxed under air-saturation for 40 h. Removal of the solvent under vacuum gave a residual solid, which was recrystallized from a mixture (1:1) of methylene chloride and petroleum ether to give 40 mg (81%) of 6a, mp 258-259 °C (mixture melting point).

II.4.5 Irradiation of (E)-1-(4,5-Diphenylimidazolyl)-1,2-dibenzoylethylene (3b). A In Benzene. A solution of 3b (500 mg, 1.13 mmol) in benzene (50 mL) was purged with nitrogen for 15 minutes and irradiated for 1.5 h. Removal of the solvent

under vacuum gave a residual solid, which was chromatographed over silica gel. Elution with petroleum ether gave 30 mg (12%) of 8, mp 109 °C (mixture melting point), after recrystallization from methanol.

Further elution with a mixture (1:1) of benzene and petroleum ether gave 100 mg (20%) of 5b, mp 223 °C, after recrystallization from a mixture (1:1) of methylene chloride and petroleum ether.

IR spectrum ν_{\max} (KBr): 3075, 3035, 2980 and 2875 (ν_{CH}), 1675 and 1660 ($\nu_{\text{C=O}}$), 1605 and 1590 ($\nu_{\text{C=C}}$) cm^{-1} .

UV spectrum λ_{\max} (methanol): 239 nm (ϵ , 36,970), 268 (39,500), and 312 (17,350).

^1H NMR spectrum (CDCl_3): δ 2.35 (dd, $J_{7a,7b} = 18$ Hz, $J_{7,7a} = 4.5$ Hz, 1 H, C-7aH), 3.20 (dd, $J_{7a,7b} = 18$ Hz, $J_{7b,8} = 6.5$ Hz, 1 H, C-7bH), 5.05 (q, 1 H, C-7H), 6.50 (q, 1 H, C-8H), and 6.90-8.25 (m, 18 H, vinylic and aromatic).

Mass spectrum, m/e (relative intensity): 454 (M^+ , 12), 452 ($\text{M}^+ - \text{H}_2$, 84), 375 ($\text{M}^+ - \text{C}_6\text{H}_5$, $-\text{H}_2$, 35), 349 ($\text{M}^+ - \text{COC}_6\text{H}_5$, 3), 347 (17), 346 (23), 242 (M^+ , $-2\text{COC}_6\text{H}_5$, -2 H, 9), 218 (19), 217 (36), 105 ($\text{C}_6\text{H}_5\text{CO}^+$, 100), and 77 (C_6H_5^+ , 89).

Anal. Calcd for $\text{C}_{31}\text{H}_{22}\text{N}_2\text{O}_2$: C, 81.94; H, 4.85; N, 6.17. Found: C, 81.76; H, 4.71; N, 6.34.

Subsequent elution of the column with a mixture (2:1) of benzene and petroleum ether gave 120 mg (24%) of 6b, mp 254 °C,

after recrystallization from a mixture (1:1) of methylene chloride and petroleum ether.

IR spectrum ν_{\max} (KBr): 3080 and 3030 (ν_{CH}), 1670 and 1660 ($\nu_{\text{C=O}}$), 1600 and 1590 ($\nu_{\text{C=C}}$) cm^{-1} .

UV spectrum λ_{\max} (methanol): 226 nm (ϵ , 32,370), and 270 (41,230).

^1H NMR spectrum (CDCl_3): δ 6.95-8.85 (m, vinylic and aromatic).

^{13}C NMR spectrum (CDCl_3): δ 113.75, 114.23, 121.34, 122.33, 122.43, 122.58, 122.76, 124.54, 125.86, 126.08, 126.73, 126.95, 127.48, 128.34, 128.58, 129.56, 130.37, 132.39, 145.62, 151.35, 153.56, 192.47 (C=O), and 193.84 (C=O).

Mass spectrum, m/e (relative intensity): 452 (M^+ , 85), 375 ($\text{M}^+ - \text{C}_6\text{H}_5$, 33), 347 ($\text{M}^+ - \text{COC}_6\text{H}_5$, 17), 346 ($\text{M}^+ - \text{COC}_6\text{H}_5$, -H, 47), 242 (11), 217 (21), 105 ($\text{C}_6\text{H}_3\text{CO}^+$, 100), 77 (C_6H_5^+ , 83).

Anal. Calcd for $\text{C}_{31}\text{H}_{20}\text{N}_2\text{O}_2$: C, 82.30; H, 4.42; N, 6.19. Found: C, 82.43; H, 4.27; N, 6.34.

Further elution of the column with benzene gave 100 mg (35%) of 1b, mp 231 $^\circ\text{C}$ (mixture melting point), after recrystallization from methanol.

B In Methanol. Irradiation of a methanol solution of 3b (500 mg, 1.13 mmol in 500 mL) for 1.5 h and workup as in the earlier case gave 50 mg (17%) of 9, mp 108 $^\circ\text{C}$ (mixture melting point), 80 mg (16%) of 5b, mp 223 $^\circ\text{C}$ (mixture melting point),

140 mg (28%) of 6b, mp 254 °C (mixture melting point), and 120 mg (41%) of 1b, mp 231 °C (mixture melting point).

II.4.6 Air-Oxidation of 5b to 6b. A benzene solution of 5b (50 mg, 0.113 mmol in 50 mL) was refluxed under air-saturation for 40 h. Removal of the solvent under vacuum and recrystallization of the residual solid from a mixture (1:1) of methylene chloride and petroleum ether gave 35 mg (76%) of 6b, 254 °C (mixture melting point).

II.4.7 Irradiation of (E)-1-(4,5-Dimethyl-2-phenylimidazolyl)-1,2-dibenzoyl-ethylene (3c). A In Benzene. A solution of 3c (500 mg, 1.23 mmol) in benzene (500 mL) was irradiated for 1 h. The irradiation was repeated several times to photolyse, in all, 3.0 g of 3c. Removal of the solvent under vacuum from the combined photolysates gave a residual solid, which was chromatographed over silica gel. Elution with petroleum ether gave 45 mg (15%) of 8, mp 109 °C (after recrystallization from methanol).

Further elution with a mixture (1:3) of benzene and petroleum ether gave 310 mg (31%) of 7c, mp 163-164 °C, after recrystallization from a mixture (1:1) of benzene and petroleum ether.

IR spectrum ν_{\max} (KBr): 3085, 3040, 2965 and 2870 (ν_{CH}), 1670 and 1655 ($\nu_{\text{C=O}}$), 1610 and 1590 ($\nu_{\text{C=C}}$) cm^{-1} .

UV spectrum λ_{\max} (methanol): 233 nm (ϵ , 27,300) and 256 (39,730).

^1H NMR spectrum (CDCl_3): δ 2.05 (s, 3 H, CH_3), 2.45 (s, 3 H, CH_3), 2.90 (d, $J = 15$ Hz, 1 H, C-6H), 4.20 (d, $J = 15$ Hz, 1 H, C-5H), and 7.10-8.25 (m, 14 H, aromatic).

Mass spectrum, m/e (relative intensity): 406 (M^+ , 7), 404 ($\text{M}^+ - \text{H}_2$, 4), 329 ($\text{M}^+ - \text{C}_6\text{H}_5$, 27), 301 ($\text{M}^+ - \text{COC}_6\text{H}_5$, 19), 300 ($\text{M}^+ - \text{COC}_6\text{H}_5$, -H, 48), 296 (8), 169 (37), 105 ($\text{C}_6\text{H}_5\text{CO}^+$, 100), 77 (C_6H_5^+ , 92).

Anal. Calcd for $\text{C}_{27}\text{H}_{22}\text{N}_2\text{O}_2$: C, 79.80; H, 5.42; N, 6.90.

Found: C, 80.11; H, 5.35; N, 6.78.

Subsequent elution of the column with benzene gave 200 mg (47%) of 1c, mp 141-142 $^\circ\text{C}$, after recrystallization from methanol.

B In Methanol. A methanol solution of 3c (200 mg, 0.49 mmol in 200 mL) was irradiated for 1 h and worked up as in the earlier case to give 75 mg (23%) of 9, mp 109 $^\circ\text{C}$ (mixture melting point), after recrystallization from methanol, 50 mg (25%) of 7c (elution with a 1:3 mixture of benzene and petroleum ether and recrystallization from a 1:1 mixture of benzene and petroleum ether), mp 163-164 $^\circ\text{C}$ (mixture melting point) and 50 mg (59%) of 1c, mp 141-142 $^\circ\text{C}$ (mixture melting point).

II.4.8 Irradiation of (E)-1-(2-Phenylbenzimidazolyl)-1,2-dibenzoyl ethylene (3d). A In Benzene. A solution of 3d (500 mg, 1.167 mmol) in benzene (500 mL) was irradiated for 1 h. Removal of the solvent under vacuum gave a residual solid which was chromatographed over silica gel. Elution with petroleum ether gave 50 mg

(18%) of 8, mp 109 °C (mixture melting point), after recrystallization from methanol

Further elution of the column with a mixture (1:3) of benzene and petroleum ether gave 65 mg (13%) of 7d, mp 206 °C, after recrystallization from a mixture (1:1) of benzene and petroleum ether.

IR spectrum ν_{\max} (KBr): 3087, 3035, 2975 and 2860 (ν_{CH}), 1670 and 1660 ($\nu_{\text{C=O}}$), 1600 and 1590 ($\nu_{\text{C=C}}$) cm^{-1} .

UV spectrum λ_{\max} (methanol): 220 nm (ϵ , 39,780), and 260 (30,360).

^1H NMR spectrum (CDCl_3): δ 3.35 (d, $J = 16$ Hz, 1 H, C-6H), 4.70 (d, $J = 16$ Hz, 1 H, C-5H) and 7.05-8.75 (m, 18 H, aromatic).

Mass spectrum, m/e (relative intensity): 428 (M^+ , 17), 426 ($\text{M}^+ - \text{H}_2$, 3), 351 ($\text{M}^+ - \text{C}_6\text{H}_5$, 15), 349 ($\text{M}^+ - \text{C}_6\text{H}_5, -\text{H}_2$, 38), 323 ($\text{M}^+ - \text{C}_6\text{H}_5\text{CO}$, 11), 322 (42), 218 (17), 192 (31), 105 ($\text{C}_6\text{H}_5\text{CO}^+$, 100), and 77 (C_6H_5^+ , 83).

Anal. Calcd for $\text{C}_{29}\text{H}_{20}\text{N}_2\text{O}_2$: C, 81.31; H, 4.67; N, 6.54.
Found: C, 81.64; H, 4.51; N, 6.60.

Further elution of the column with benzene gave 115 mg (58%) of 1d, mp 288-289 °C (mixture melting point), after recrystallization from 75% ethanol.

Subsequent elution of the column with a mixture (4:1) of benzene and ethyl acetate gave 50 mg (9%) of 2-(1-(2-phenylbenzimidazolyl))-4-phenoxy-4-phenyl-3-butenic acid (10d),

mp 270-271 °C, after recrystallization from 1:1 mixture of ethyl acetate and benzene

IR spectrum ν_{max} (KBr): 3060, 3025 and 2982 (ν_{CH}), 3000-2500 (ν_{OH}), 1742 ($\nu_{\text{C=O}}$), 1635 and 1590 ($\nu_{\text{C=C}}$) cm^{-1} .

UV spectrum λ_{max} (methanol): 253 nm (ϵ , 48,730).

^1H NMR spectrum (CDCl_3): δ 5.90 (d, $J = 8$ Hz, 1 H, D_2O -exchangeable, methine proton), 6.45 (d, $J = 8$ Hz, 1 H, vinylic), 7.10-8.35 (m, 19 H, aromatic), and 7.85 (broad s, D_2O -exchangeable, 1 H, OH).

Mass spectrum, m/e (relative intensity): 446 (M^+ , 2), 429 ($\text{M}^+ - \text{OH}$, 100), 428 ($\text{M}^+ - \text{H}_2\text{O}$, 13), 401 ($\text{M}^+ - \text{CO}_2\text{H}$, 34), 336 ($\text{M}^+ - \text{OH}$, $-\text{OC}_6\text{H}_5$, 73), 193 (87), 93 (49), and other peaks.

Anal. Calcd for $\text{C}_{29}\text{H}_{22}\text{N}_2\text{O}_3$: C, 78.03; H, 4.91; N, 6.28.

Found: C, 78.31; H, 4.78; N, 6.12.

B In Methanol A solution of 3d (500 mg, 1.167 mmol) in methanol (500 mL) was irradiated for 1 h and worked up by removing the solvent under vacuum and chromatographing the residual solid over silica gel. Elution with a mixture (1:9) of benzene and petroleum ether gave 85 mg (27%) of 9, mp 108 °C (mixture melting point), after recrystallization from methanol.

Further elution of the column with a 1:4 mixture of benzene and petroleum ether gave 80 mg (14%) of methyl 2-(2-phenylbenzimidazolyl)-4-phenoxy-4-phenyl-3-butenate (11d), mp 158 °C, after recrystallization from cyclohexane.

IR spectrum ν_{\max} (KBr): 3075, 3025, 2978 and 2840 (ν_{CH}), 1745 ($\nu_{\text{C=O}}$), 1638 and 1595 ($\nu_{\text{C=C}}$) cm^{-1} .

UV spectrum λ_{\max} (methanol): 248 nm (ϵ , 50,780).

Mass spectrum, m/e (relative intensity): 460 (M^+ , 2), 445 ($M^+ - \text{CH}_3$, 3), 429 ($M^+ - \text{OCH}_3$, 100), 428 ($M^+ - \text{CH}_3\text{OH}$, 36), 401 (38), 336 ($M^+ - \text{OCH}_3$, $-\text{OC}_6\text{H}_5$, 11), 193 (88), 93 (50), and 77 (73).

Anal. Calcd for $\text{C}_{30}\text{H}_{24}\text{N}_2\text{O}_3$: C, 78.26; H, 5.22; N, 6.09.

Found: C, 78.38; H, 5.34; N, 5.89.

Subsequent elution of the column with a mixture (1:3) of benzene and petroleum ether gave 40 mg (8%) of 7d, mp 206 °C (mixture melting point), after recrystallization from a mixture (1:1) of benzene and petroleum ether.

Continued elution of the column with benzene gave 135 mg (65%) of 1d, mp 288-289 °C (mixture melting point), after recrystallization from ethanol.

II.4.9 Reaction of 10d with Diazomethane. To a stirred solution of 10d (50 mg, 0.11 mmol) in ether (5 mL) was added an ether solution of diazomethane (1 mL, 5%) at 0 °C and the stirring was continued for 1 h. Removal of the solvent under vacuum and recrystallization of the product from cyclohexane gave 35 mg (68%) of 11d, mp 156-157 °C (mixture melting point).

II.4.10 Irradiation of (Z)-1-(2-Phenylbenzimidazolyl)-1,2-dibenzoyl ethylene (4d). A solution of 4d (500 mg, 1.167 mmol)

in benzene (500 mL) was irradiated for 1 h and worked up in the usual manner by removal of the solvent under vacuum and chromatographing the residual mixture over silica gel to give 40 mg (14%) of 8, mp 109 °C (mixture melting point) (elution with petroleum ether and recrystallization from methanol), 40 mg (8%) of 7d, mp 206 °C (mixture melting point) (elution with a 1:4 mixture of benzene and petroleum ether), 70 mg (14%) of the unchanged starting material (4d), mp 170 °C (mixture melting point) (elution with a 1:3 mixture of benzene and petroleum ether and recrystallization from methanol), 100 mg (20%) of the E isomer 3d, mp 197-198 °C (mixture melting point) (elution with a 1:1 mixture of benzene and petroleum ether and recrystallization from methanol) and 100 mg (43%) of 1d, mp 288-289 °C (mixture melting point), recrystallization from ethanol.

II.4.11 Irradiation of (E)-1-Benzimidazolyl-1,2-dibenzoyl-ethylene (3e). A In Benzene. A benzene solution of 3e (500 mg, 1.42 mmol, in 500 mL) was irradiated for 1 h and worked up by removing the solvent under vacuum and chromatographing the product mixture over silica gel. Elution with petroleum ether gave 60 mg (18%) of 8, mp 109 °C (mixture melting point), after recrystallization from methanol.

Further elution with benzene gave 60 mg (56%) of 1e, mp 172 °C (mixture melting point), after recrystallization from ethanol. Subsequent elution of the column with a mixture (4:1) of benzene and ethyl acetate gave 100 mg (19%) of 2-benzimidazolyl-

4-phenoxy-4-phenyl-3-butenic acid (10e), mp 264-265 °C, after recrystallization from a mixture (1:1) of benzene and ethyl acetate.

IR spectrum ν_{max} (KBr): 3080 and 3030 (ν_{CH}), 3000-2500 (ν_{OH}), 1745 ($\nu_{\text{C=O}}$), 1630 and 1590 ($\nu_{\text{C=C}}$) cm^{-1} .

UV spectrum λ_{max} (methanol): 256 nm (ϵ , 38,760).

^1H NMR spectrum (CDCl_3): δ 5.45 (d, $J=9$ Hz, 1 H, D_2O -exchangeable, methine), 6.35 (d, $J=9$ Hz, 1 H, vinylic), 7.0-7.55 (m, 15 H, aromatic), and 7.85 (s, 1 H, D_2O -exchangeable, OH).

Mass spectrum, m/e (relative intensity): 370 (M^+ , 3), 353 ($\text{M}^+ - \text{OH}$, 100), 352 ($\text{M}^+ - \text{H}_2\text{O}$, 23), 325 ($\text{M}^+ - \text{CO}_2\text{H}$, 34), 260 ($\text{M}^+ - \text{OH}$, $-\text{OC}_6\text{H}_5$, 26), 117 (88), 93 (73), and 77 (81).

Anal. Calcd for $\text{C}_{23}\text{H}_{18}\text{N}_2\text{O}_3$: C, 74.59; H, 4.86; N, 7.57.

Found: C, 74.37; H, 4.66; N, 7.69.

B In Methanol. A methanol solution of 3e (500 mg, 1.42 mmol in 500 mL) was irradiated for 1 h and worked up by removal of the solvent under vacuum and chromatographing the residual solid over silica gel. Elution with a mixture (1:9) of benzene and petroleum ether gave 80 mg (21%) of 9, mp 108 °C (mixture melting point), after recrystallization from methanol.

Further elution with a mixture (1:3) of benzene and petroleum ether gave 125 mg (22%) of methyl 2-(1-benzimidazolyl)-4-phenoxy-4-phenyl-3-butenate (11e), mp 166 °C, after recrystallization from cyclohexane.

IR spectrum ν_{\max} (KBr): 3075, 3030, 2965, and 2850 (ν_{CH}), 1745 ($\nu_{\text{C=O}}$), 1635 and 1595 ($\nu_{\text{C=C}}$) cm^{-1} .

UV spectrum λ_{\max} (methanol): 246 nm (ϵ , 47,570).

^1H NMR spectrum (CDCl_3): δ 3.70 (s, 3 H, OCH_3), 5.40 (d, $J = 9$ Hz, 1 H, D_2O -exchangeable, methine), 6.30 (d, $J = 9$ Hz, 1 H, vinylic), 7.05-7.55 (m, 15 H, aromatic).

Mass spectrum, m/e (relative intensity): 384 (M^+ , 3), 369 ($\text{M}^+ - \text{CH}_3$, 8), 354 (77), 353 ($\text{M}^+ - \text{CCH}_3$, 100), 352 ($\text{M}^+ - \text{CH}_3\text{OH}$, 33), 325 (5), 291 (7), 260 (21), 117 (89), 93 (70).

Anal. Calcd for $\text{C}_{24}\text{H}_{20}\text{N}_2\text{O}_3$: C, 75.00; H, 5.21; N, 7.29.

Found: C, 75.23; H, 5.34; N, 7.18, and other peaks.

Continued elution of the silica gel column with benzene gave 100 mg (59%) of 1e, mp 172 $^\circ\text{C}$ (mixture melting point), after recrystallization from ethanol.

II.4.12 Reaction of 2-(1-Benzimidazolyl)-4-phenoxy-4-phenyl-3-butenic acid (10c) with Diazomethane. To a stirred solution of 10c in ether (30 mg, 0.12 mmol in 5 mL) was added an ether solution of diazomethane (1 mL, 5%) at 0 $^\circ\text{C}$ and the stirring was continued for an additional hour. Removal of the solvent under vacuum and recrystallization of the product from cyclohexane gave 30 mg (72%) of 11e, mp 116 $^\circ\text{C}$ (mixture melting point).

II.4.13 Laser Flash Photolysis.¹⁹ Pulse excitation was carried out at 337.1 nm (2-3 mJ, ~ 8 ns), employing a UV 400 Molelectron Nitrogen laser or at 308 and 248 nm (~ 40 mJ, defocussed,

20 ns), employing a Lambda-Physik MSC 101 excimer laser. The transient phenomena were studied using a kinetic spectrometer, described elsewhere.²⁹ The solvents employed were benzene and methanol and unless oxygen effects were meant to be studied, the solutions were deoxygenated by purging with argon or nitrogen. In experiments where a large number of laser shots were necessary, e.g., for wavelength-by-wavelength measurements of transient absorption spectra, a flow system was used in which the solutions for photolysis were allowed to drain from a reservoir through a cell.

II.4.14 Pulse Radiolysis.¹⁹ The pulse radiolysis experiments were performed, employing 7 MeV electron pulses (5 ns) from the Notre Dame ARCO-LP-7 linear accelerator in the computer controlled apparatus, described elsewhere.³⁰

II.5 REFERENCES

- (1) G. W. Griffin and E. J. O'Connell, J. Am. Chem. Soc. 84, 4148-4149 (1962).
- (2) H. E. Zimmerman, H. G. C. Durr, R. G. Lewis and S. Braun, J. Am. Chem. Soc. 84, 4149-4150 (1962).
- (3) A. Padwa, D. Crumrine and A. Shubber, J. Am. Chem. Soc. 88, 3064-3069 (1966).
- (4) N. Sugiyama and C. Kashima, Bull. Chem. Soc. Jpn. 43, 1875-1877 (1970).
- (5) H.E. Zimmerman, H. G. C. Durr, R. S. Givens and R. G. Lewis, J. Am. Chem. Soc. 89, 1863-1874 (1967).
- (6) S. Lahiri, V. Dabral, S. M. S. Chauhan, E. Chakachery, C. V. Kumar, J. C. Scaino and M. V. George, J. Org. Chem. 45, 3782-3790 (1980).
- (7) B. A. R. C. Murty, C. V. Kumar, V. Dabral, P. K. Das and M. V. George, J. Org. Chem. 49, 4165-4171 (1984).
- (8) B. A. R. C. Murty, Ph.D. Thesis, Indian Institute of Technology, Kanpur, 1982.
- (9) C. V. Kumar, B. A. R. C. Murty, S. Lahiri, E. Chackachery, J. C. Scalano and M. V. George, J. Org. Chem. 49, 4923-4929 (1984).
- (10) C. V. Kumar, Ph.D. Thesis, Indian Institute of Technology, Kanpur, 1981.
- (11) B. A. R. C. Murty, S. Pratapan, C. V. Kumar, P. K. Das and M. V. George, J. Org. Chem. 50, 2533-2538 (1985).

- 12) B. B. Lohray, C. V. Kumar, P. K. Das and M. V. George, J. Org. Chem. 49, 4647-4656 (1984).
- 13) B. B. Lohray, Ph.D. Thesis, Indian Institute of Technology, Kanpur, 1983.
- 14) R. Barik, C. V. Kumar, P. K. Das and M. V. George, J. Org. Chem. 50, 4309-4317 (1985).
- 15) J. E. Dolfini, J. Org. Chem. 30, 1298-1300 (1965).
- 16) S. Lahiri, M. P. Mahajan, R. Prasad and M. V. George, Tetrahedron 33, 3159-3170 (1977).
- 17) R. Barik, K. Bhattacharyya, P. K. Das and M. V. George, J. Org. Chem., Under publication.
- 18) For some examples of the photocyclizations of stilbene derivatives, see F. R. Stermitz, 'Organic Photochemistry;' O. L. Chapman, Ed.; Marcel Dekker: New York, Vol. 1, pp. 247-282 (1967).
- 19) All laser flash photolysis and pulse radiolysis studies have been carried out by Dr. P. K. Das, Dr. K. Bhattacharyya and Professor M. V. George at the Radiation Laboratory of the University of Notre Dame (USA).
- 20) (a) R. Bensasson and E. J. Land, Photochem. Photobiol. Rev. 3, 163-191 (1978); (b) R. Bensasson and E. J. Land, Trans. Faraday Soc. 67, 1904-1915 (1971); (c) E. J. Land, Proc. Royal Soc. London, Ser. A A305, 459-471 (1968).
- 21) D. Davidson, M. Weiss and M. Jelling, J. Org. Chem. 2, 319-327 (1937).
- 22) W. B. Leslie and G. W. Watt, J. Org. Chem. 7, 73-78 (1942).

- 23) F. R. Japp and W. P. Wynne, J. Chem. Soc. 49, 462-471 (1986).
- 24) K. Bernhauer and R. Hoffmann, J. Prakt. Chem. 149, 321-323 (1937); Chem. Abstr. 32, 497-498 (1938).
- 25) B. A. Porai-Koshits, O. F. Ginsburg and L. S. Efros, J. Gen. Chem. (U.S.S.R.) 17, 1768-1773 (1947); Chem. Abstr. 42, 5903 (1948).
- 26) A. I. Vogel, 'A Textbook of Practical Organic Chemistry,' English Language Book Society and Longman Group Ltd., London, pp. 853 (1973).
- 27) R. E. Lutz and Jr., W. R. Smithy, J. Org. Chem. 16, 51-56 (1951).
- 28) R. E. Lutz, 'Organic Synthesis,' E. C. Horning Ed., John Wiley and Sons, Inc.: New York, Coll. Vol. 3, pp. 248-250 (1955).
- 29) P. K. Das, M. V. Encinas, R. D. Small Jr., and J. C. Scaiano, J. Am. Chem. Soc. 101, 6965-6970 (1979); (b) P. K. Das and K. Bobrowski, J. Chem. Soc. Faraday Trans. 2, 77, 1009-1027 (1981); (c) S. K. Chattopadhyay, P. K. Das and G. Hug, J. Am. Chem. Soc. 104, 4507-4514 (1982).
- 30) L. K. Patterson and J. Lillie, Int. J. Radiat. Phy. Chem. 6, 129-141 (1974).

CHAPTER III

PHOTOTRANSFORMATIONS OF 1-TRIAZOLYL-1,2-DIBENZOYL- ALKENES AND RELATED SUBSTRATES

III.1 ABSTRACT

The photochemical transformations of a number of 1-(1,2,3- and 1,2,4-triazolyl)-1,2-dibenzoylalkenes (3, 4, 8 and 9) and 1-benzotriazolylethylene-1,2-dicarboxylates (5 and 6) have been investigated under steady-state photolysis. Laser flash photolysis of these substrates have been carried out to study their transient behaviour. The substrates under examination include (E)-1-benzotriazolyl-1,2-dibenzoylethylene (3), (Z)-1-benzotriazolyl-1,2-dibenzoylethylene (4), dimethyl 1-benzotriazolylmaleate (5), dimethyl 1-benzotriazolylfumarate (6), (E)-1-(3,5-diphenyl-1H-1,2,4-triazolyl)-1,2-dibenzoylethylene (8), and (Z)-1-(3,5-diphenyl-1H-1,2,4-triazolyl)-1,2-dibenzoylethylene (9). Product analysis revealed that several types of photo-reactions are involved depending on the nature of the substituents on the ethylenic moieties of these substrates. The benzotriazolyl-1,2-dibenzoylethylenes 3 and 4, upon steady-state

irradiation, undergo a variety of reactions such as intramolecular phenyl ring migration leading to the ketene derived acid 12a or ester 12b, photochemical nitrogen loss and subsequent rearrangement of the resultant biradical intermediates giving rise to the benzazepinone derivatives 11 and 14, respectively and also the formation of the bisbenzotriazolylbutane-1,4-dione derivatives 13 and 15, respectively. Irradiation of the corresponding maleate 5 and the fumarate 6, on the other hand, led to the generation of the diradical intermediate 24 through a nitrogen elimination process, which on subsequent reaction with solvent, gave rise to the products such as 16 and 17, in addition to the cis-trans photoisomerization of the olefinic double bonds. In contrast, the 1-(1H-1,2,4-triazolyl)-1,2-dibenzoylthylenes 8 and 9, under similar conditions, underwent electrocyclic ring-closure reactions, giving rise to the dihydroisoquinoline derivatives 19b and 19a, respectively, and also photofragmentation reactions, resulting in the loss of triazolyl moieties from the parent dibenzoylalkenes. Laser flash photolysis, in several cases, revealed transient processes related to ketene and zwitter-ionic intermediates.

III.2 INTRODUCTION

In recent years, the phototransformations of several substrates containing 1,2-dibenzoylalkene moieties such as 1,4- and 1,2-epoxy compounds,^{1,2} dibenzobarrelenes,³⁻⁵ 1-pyrazolyl-1,2-dibenzoylalkenes,^{6,7} 1-aziridinyl-1,2-dibenzoylalkenes,⁸

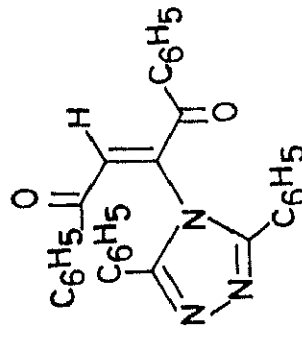
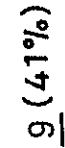
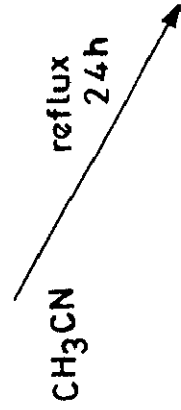
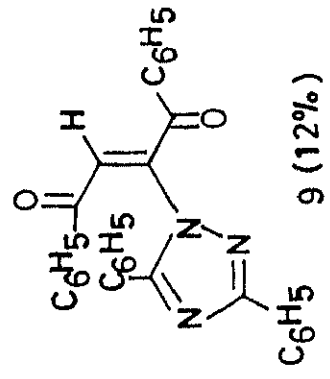
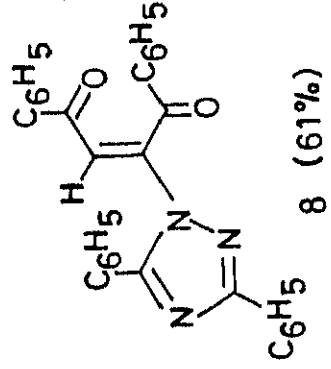
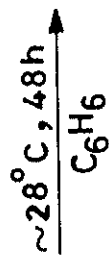
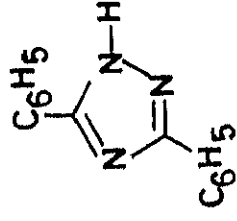
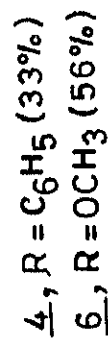
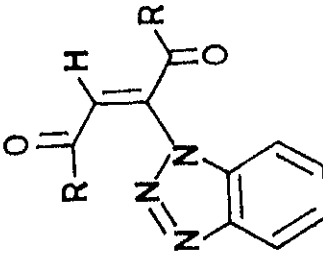
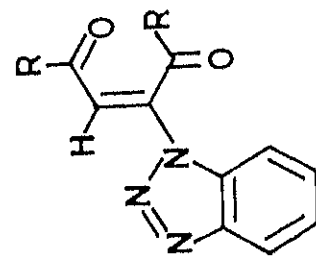
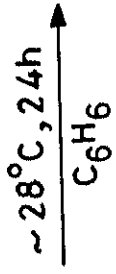
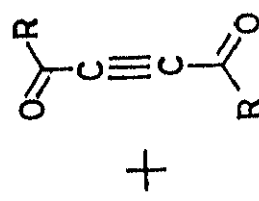
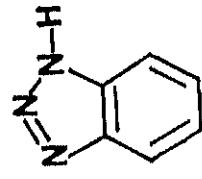
and 1-imidazolyl-1,2-dibenzoylalkenes⁹ have been reported from this laboratory. It has been observed that, in general, the photorearrangements of 1,2-dibenzoylalkenes are strongly influenced by the nature of the substituents present in them.

The object of the present investigation has been to examine the phototransformations of some selected triazolyl-1,2-dibenzoylalkenes and related substrates, capable of undergoing multipathway photoreactions. The substrates that we have examined include the dibenzoylethylenes, 3, 4, 8 and 9, the benzotriazolylmaleate 5 and the benzotriazolylfumarate 6.

III.3 RESULTS AND DISCUSSION

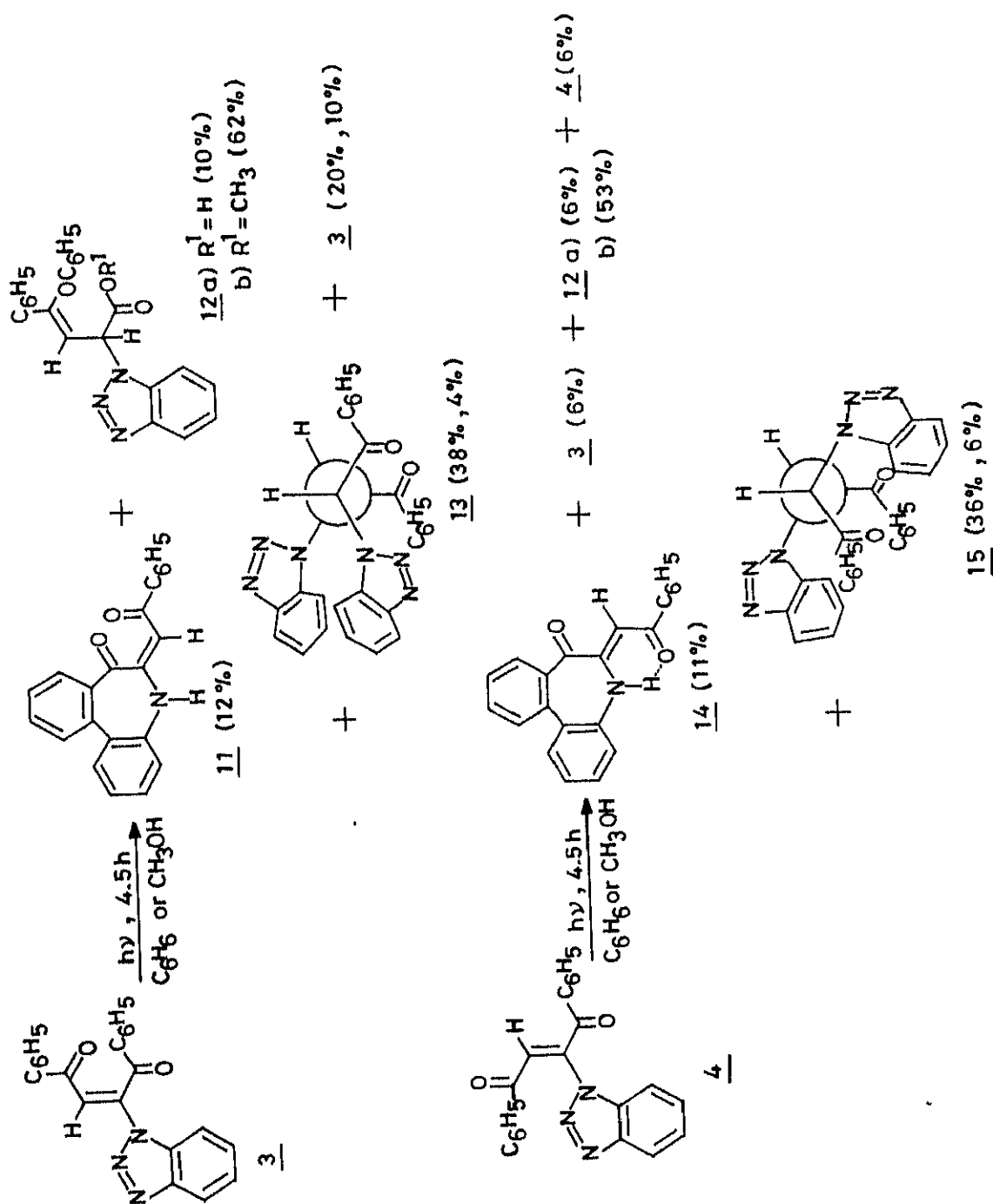
III.3.1 Preparation of the Starting Materials. The benzotriazolyl-1,2-dibenzoylethylenes 3 and 4, the benzotriazolylmaleate 5 and the benzotriazolylfumarate 6 were prepared by the reaction of benzotriazole (1) with dibenzoylacetylene (DBA, 2a) and dimethyl acetylenedicarboxylate (DMAD, 2b), respectively, in refluxing benzene. The (E)- and (Z)-1-(1H-1,2,4-triazolyl)-1,2-dibenzoylethylenes 8 and 9 were prepared by the reaction of 3,5-diphenyl-1H-1,2,4-triazole (7) with 2a in benzene or acetonitrile (Scheme III.1). The structures of all these adducts have been determined on the basis of analytical results and spectral data.

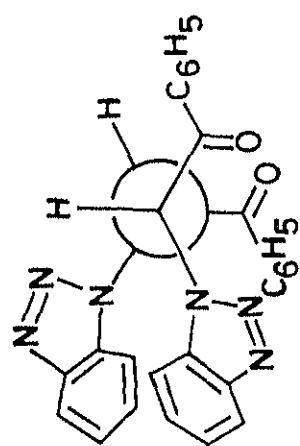
III.3.2 Preparative Photochemistry and Product Identification. Irradiation of (E)-1-benzotriazolyl-1,2-dibenzoyl-



ethylene (3) in benzene gave a mixture of the meso-bisbenzotriazolylobutanedione 13 (38%), the benzazepinone 11 (12%), and the butenoic acid 12a (10%), along with some recovered starting material (3, 20%). Similarly, the irradiation of 4 in benzene gave a mixture of the d,l-bisbenzotriazolylobutanedione 15 (36%), the benzazepinone 14 (11%), the butenoic acid 12a (6%), and the E isomer 3 (6%), along with some recovered starting material (4, 6%) (Scheme III.2). Irradiation of 3 in methanol, on the other hand, gave a mixture of the methyl butenoate 12b (62%), 13 (4%) and some recovered starting material (3, 12%). Similar results were obtained in the irradiations of 4 in methanol. The structures of all the photoproducts 11-15 were established on the basis of analytical results, spectral data and chemical evidence. The ^1H NMR spectrum of 13, for example, showed a singlet at δ 5.32 (2 H) and a multiplet at δ 7.05-8.15 (13 H) assigned to the methine and aromatic protons, respectively (Figure III.1). Similarly, the ^1H NMR spectrum of 15 showed a singlet at δ 7.65 (2 H) and a multiplet at δ 7.15-8.05 (13 H) (Figure III.2). The downfield chemical shift of the methine protons of 15 would suggest that it is the d,l-isomer, whereas the relatively upfield δ -value of the methine protons of 13 would suggest that it is the meso-isomer.¹⁰ It was observed that treatment of 13 with trimethylamine gave a mixture of 15 (55%) and unchanged starting material 13 (25%), indicating that the d,l-isomer 15 is relatively more stable than the meso-isomer 13. Further confirmation of the structure of 13 was derived

Scheme III.2





13

methine
5.32

TMS

0.0

4.0

5.0

6.0

7.0

8.0

9.0

← PPM (δ)

Figure III.1 1H NMR spectrum (90 MHz) of **13**.

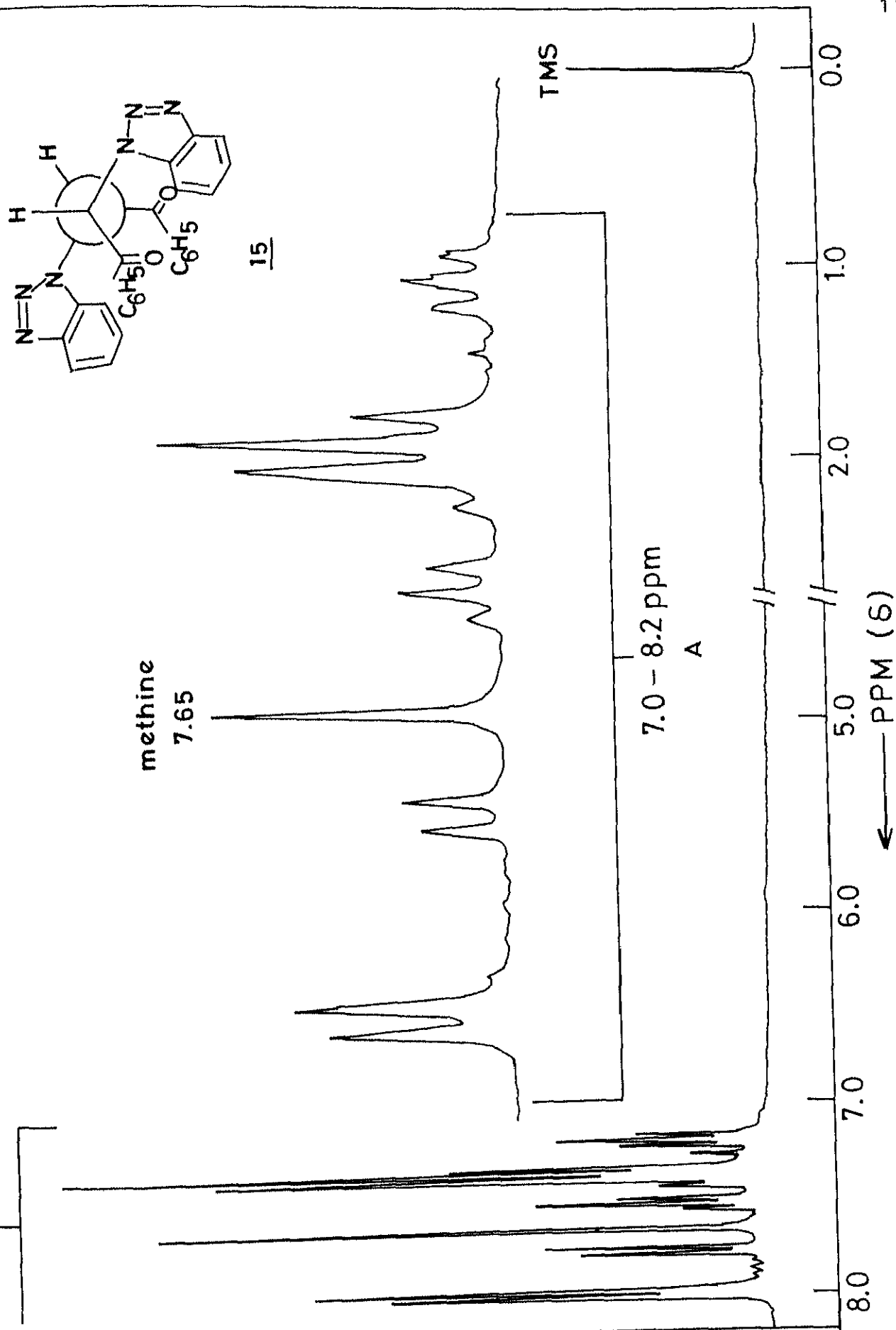


Figure III.2 ^1H NMR spectrum (270 MHz) of **15**.

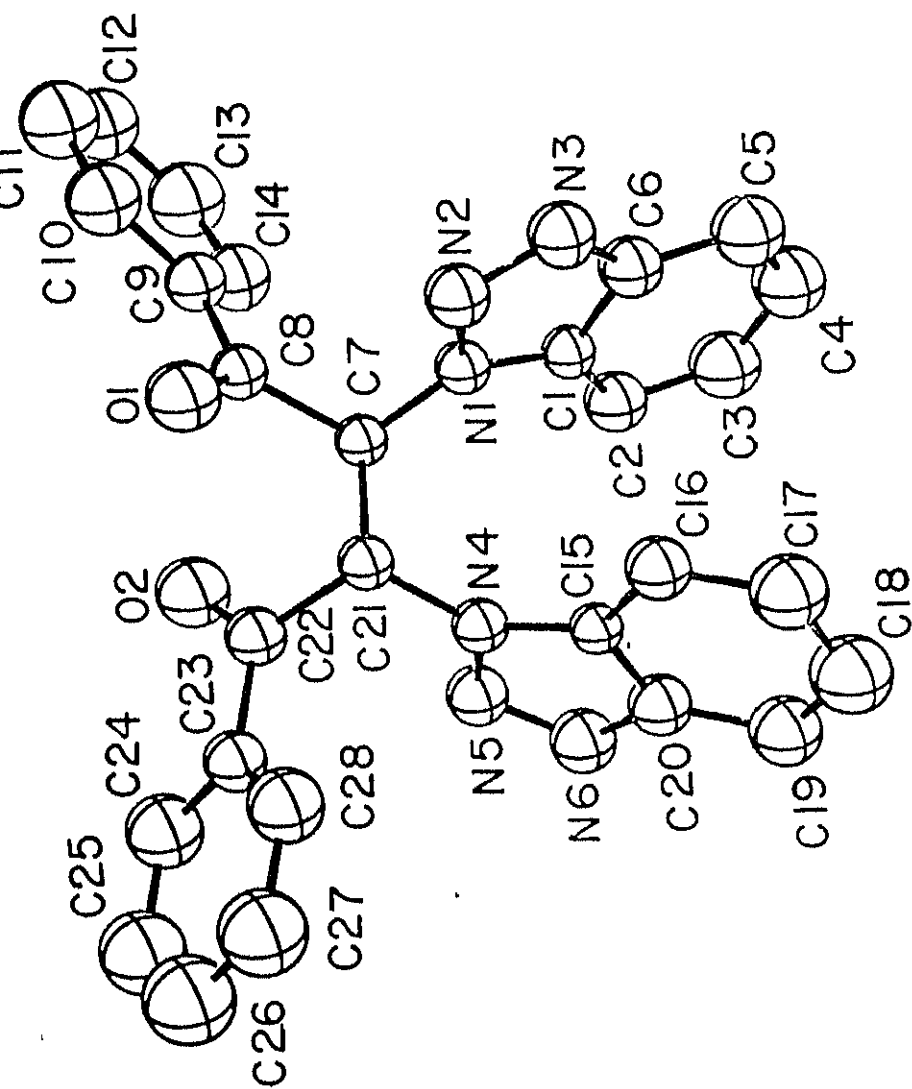


Figure III.3 Computer-generated drawing of 13 derived from the X-ray coordinates with hydrogen omitted for clarity.

through X-ray crystallographic analysis (Figure III.3).

The ^1H NMR spectrum of the benzazepinone 11 showed a singlet at δ 6.85 (1 H) which could be assigned to its exovinylic proton, whereas its aromatic and NH protons appeared at δ 7.00-8.05 (m, 13 H) and δ 10.25 (s, 1 H, D_2O -exchangeable), respectively (Figure III.4). Similarly, the ^1H NMR spectrum of 14 showed a singlet at δ 7.00 (1 H, vinylic), a multiplet at δ 7.15-8.20 (13 H, aromatic) and a broad singlet at δ 10.45 (1 H, D_2O -exchangeable, NH) (Figure III.5). Confirmation of the structural assignments for 11 and 14 was derived through the conversion of 11 to the more stable isomer 14, on refluxing in methanol or treatment with triethylamine.

The ^1H NMR spectral data of the butenoic acid 12a and the ester 12b are in agreement with their structural assignments. Further confirmation was derived through the conversion of 12a to 12b, on treatment with diazomethane.

Irradiation of the triazolylmaleate 5 in benzene gave a mixture of dimethyl indole-2,3-dicarboxylate (17, 50%), dimethyl 1-(2-phenylanilino)fumarate (16, 4%) and the triazolylfumarate 6 (16%), along with some recovered starting material 5 (12%). Irradiation of the benzotriazolylfumarate 6 in benzene gave a mixture of the indole derivative 17 (58%), the 1-(2-phenylanilino)-fumarate 16 (3%), the triazolylmaleate 5 (6%) and unchanged starting material 6 (18%). The structure of 16 has been arrived at on the basis of analytical results and spectral data, whereas

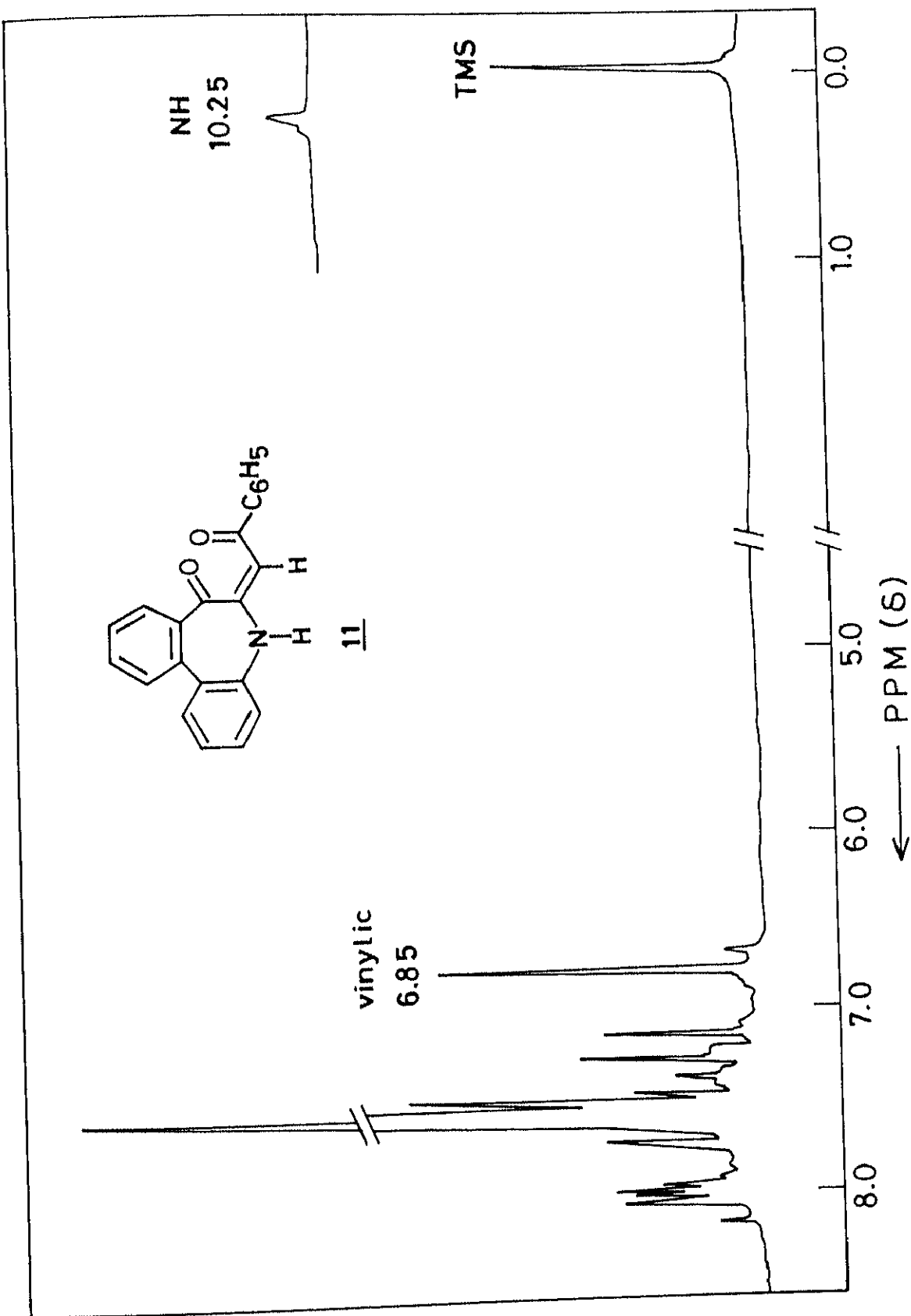
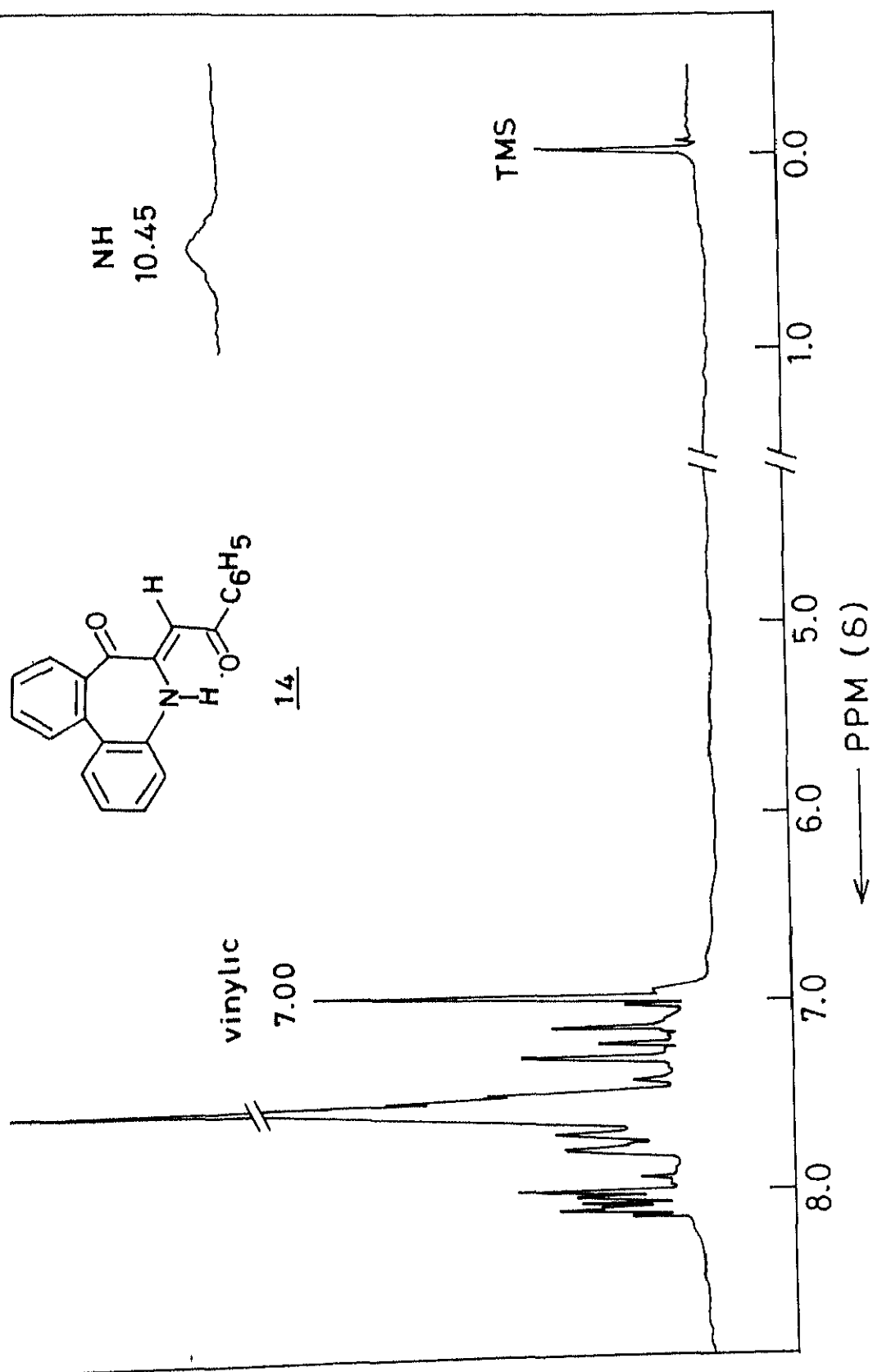
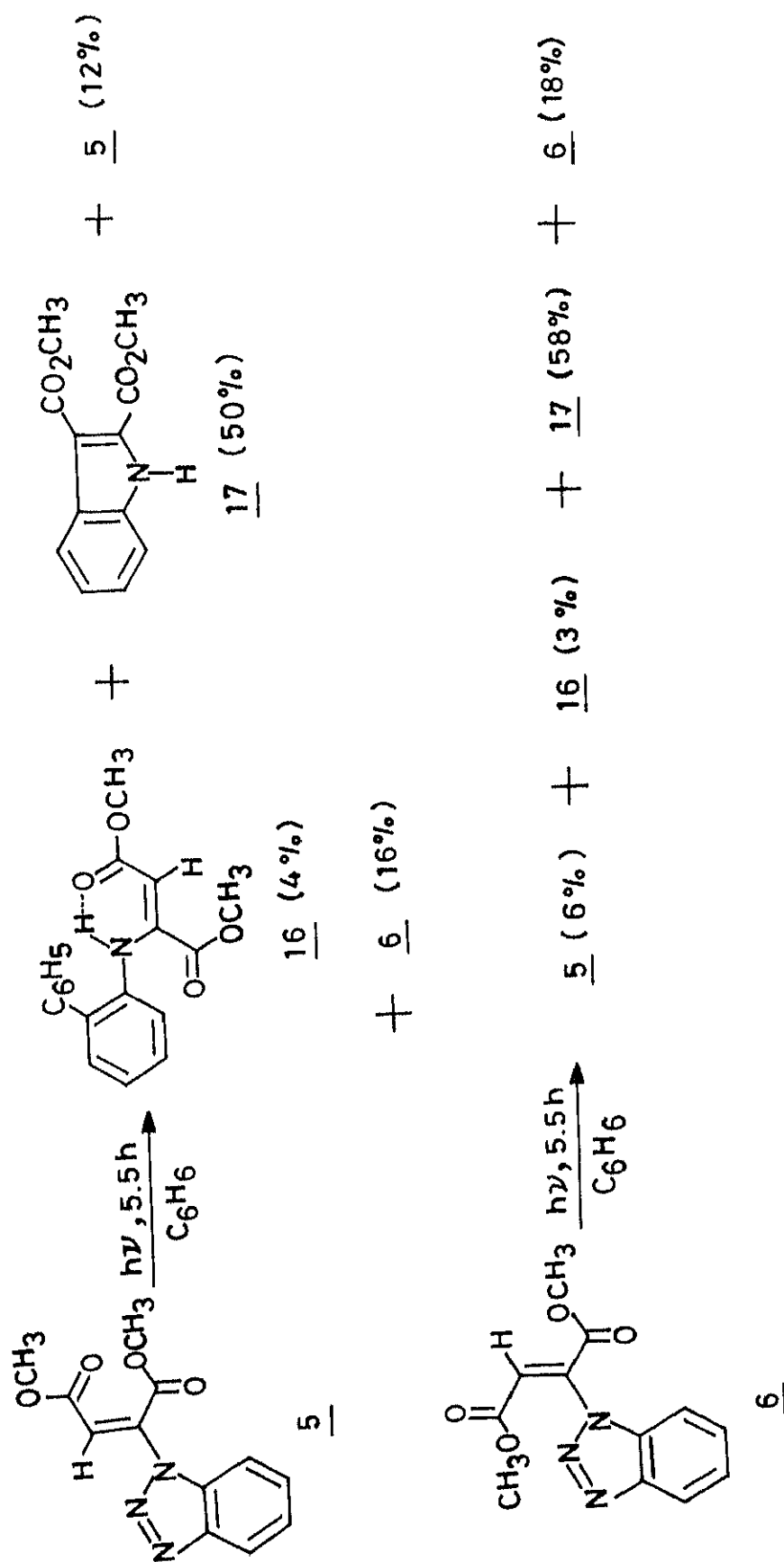


Figure III.4 ^1H NMR spectrum (90 MHz) of **11**.

Figure III.5 ^1H NMR spectrum (90 MHz) of **14**.

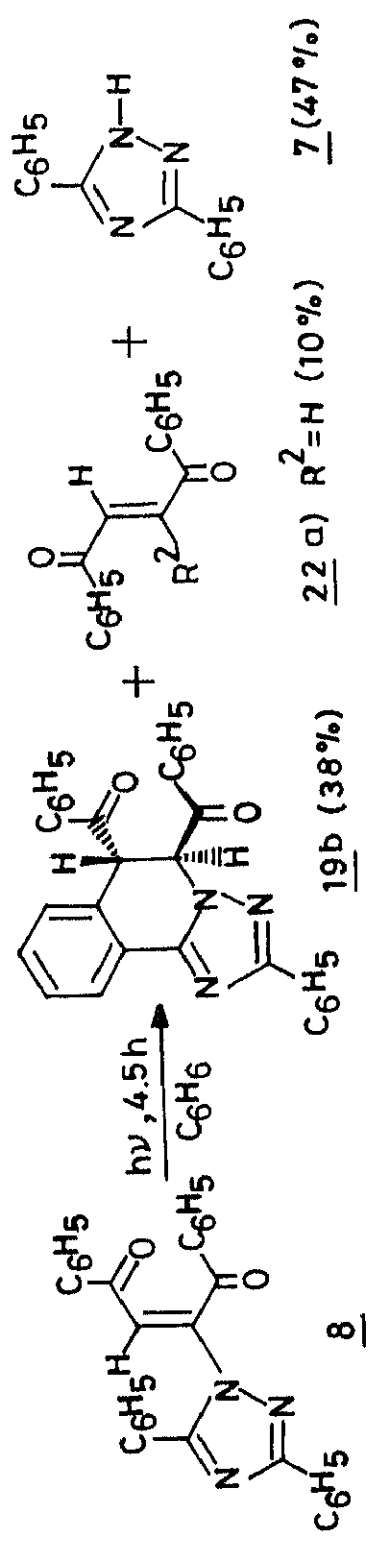
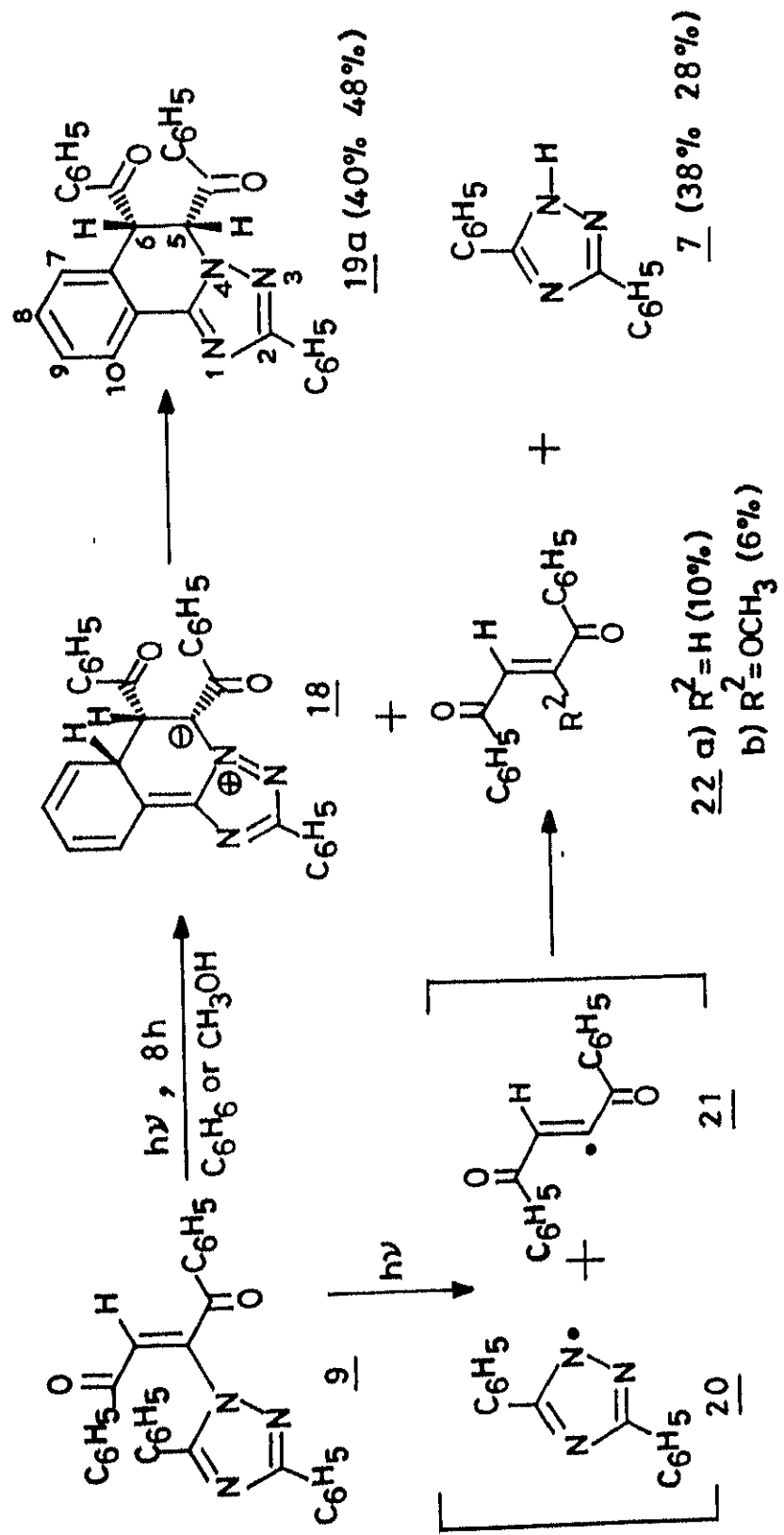
Scheme III.3



the structure of 17 has been confirmed through comparison with an authentic sample.¹¹

In contrast, the irradiation of (Z)-1-(3,5-diphenyl-1H-1,2,4-triazolyl)-1,2-dibenzoylethylene (9) in benzene gave a mixture of the errythro-dihydrotriazoloisoquinoline derivative 19a (40%), trans-1,2-dibenzoylethylene (22a, 10%) and 3,5-diphenyl-1,2,4-triazole (7, 38%). Irradiation of 9 in methanol gave a mixture of 19a (48%), 7 (28%) and trans-1,2-dibenzoyl-1-methoxyethylene (22b, 6%). The irradiation of (E)-1-(3,5-diphenyl-1H-1,2,4-triazolyl)-1,2-dibenzoylethylene (8) in benzene, on the other hand, gave a mixture of the threo-dihydrotriazoloisoquinoline 19b (38%), trans-1,2-dibenzoylethylene (22a, 10%) and the triazole 7 (47%). The ¹H NMR spectrum of 19a showed two doublets at δ 5.15 ($J = 5$ Hz, 1 H) and δ 6.25 ($J = 5$ Hz, 1 H) assigned to the two methine protons at C-6 and C-5 positions, respectively, whereas the aromatic protons appeared as a multiplet centered at δ 7.65 (19 H) (Figure III.6). Similarly, the ¹H NMR spectrum of 19b showed two doublets at δ 3.75 ($J = 16$ Hz, 1 H, methine), and δ 4.95 ($J = 16$ Hz, 1 H, methine), and a multiplet at δ 7.10-8.35 (19H, aromatic) (Figure III.7). The ¹H NMR spectral assignments of 19a and 19b were in agreement with those of dihydroisoquinoline derivatives observed in the phototransformation of 1-pyrazolyl-1,2-dibenzoylalkenes,⁶ and 1-imidazolyl-1,2-dibenzoylalkenes.⁹

III.3.3 Discussion. Product analysis revealed that four major pathways are operative in the photochemistry of the



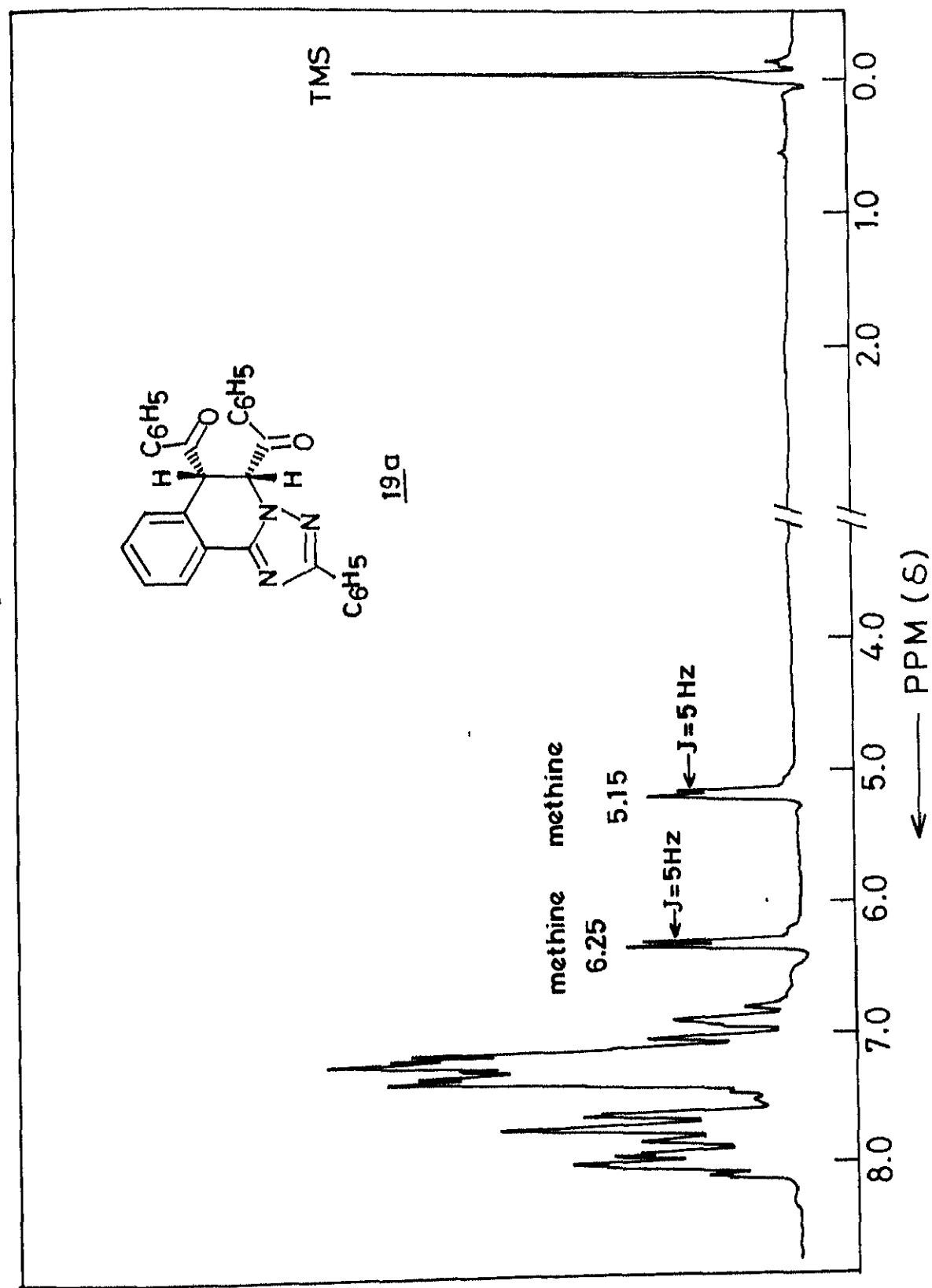


Figure III.6 ^1H NMR spectrum (80 MHz) of 19a.

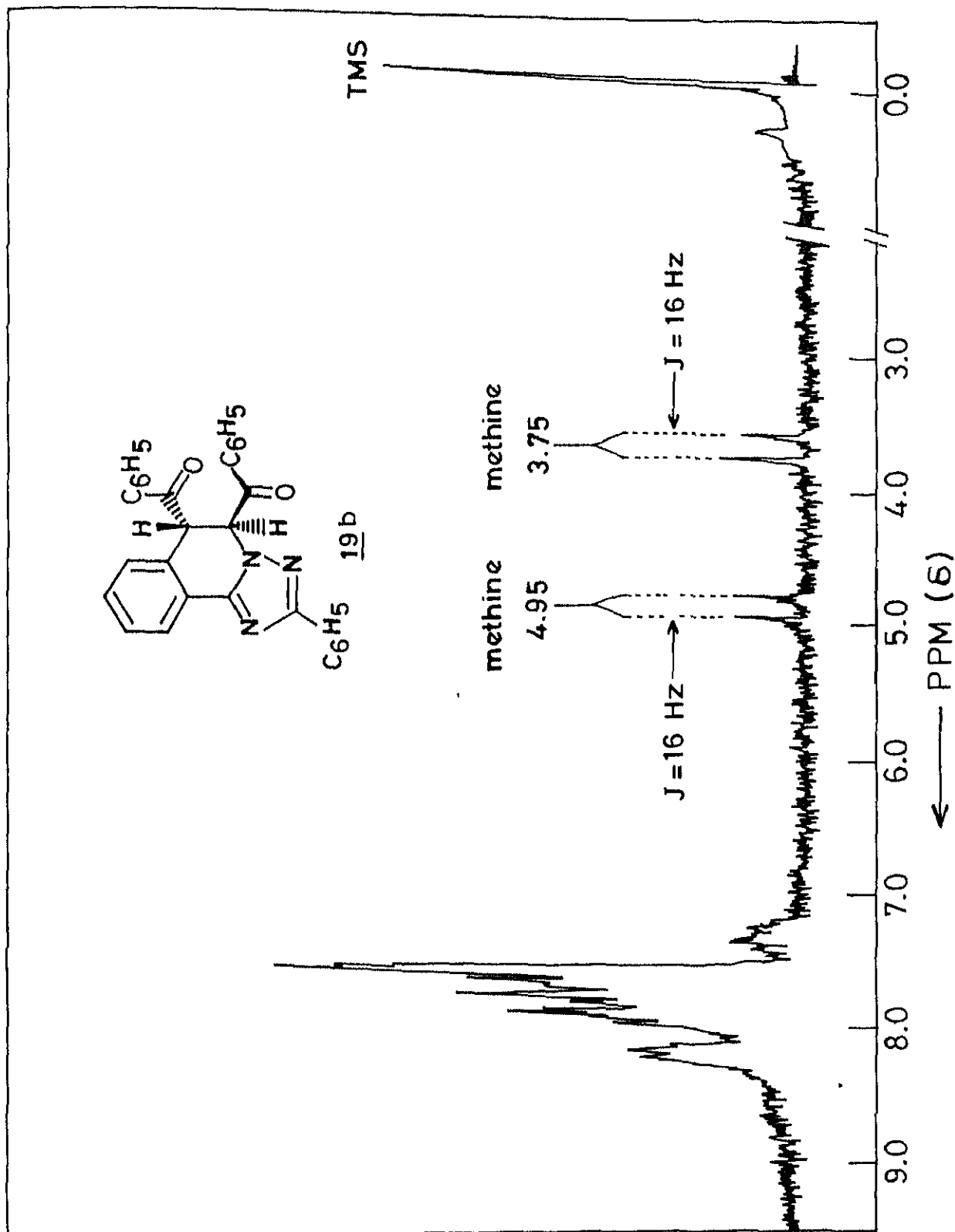
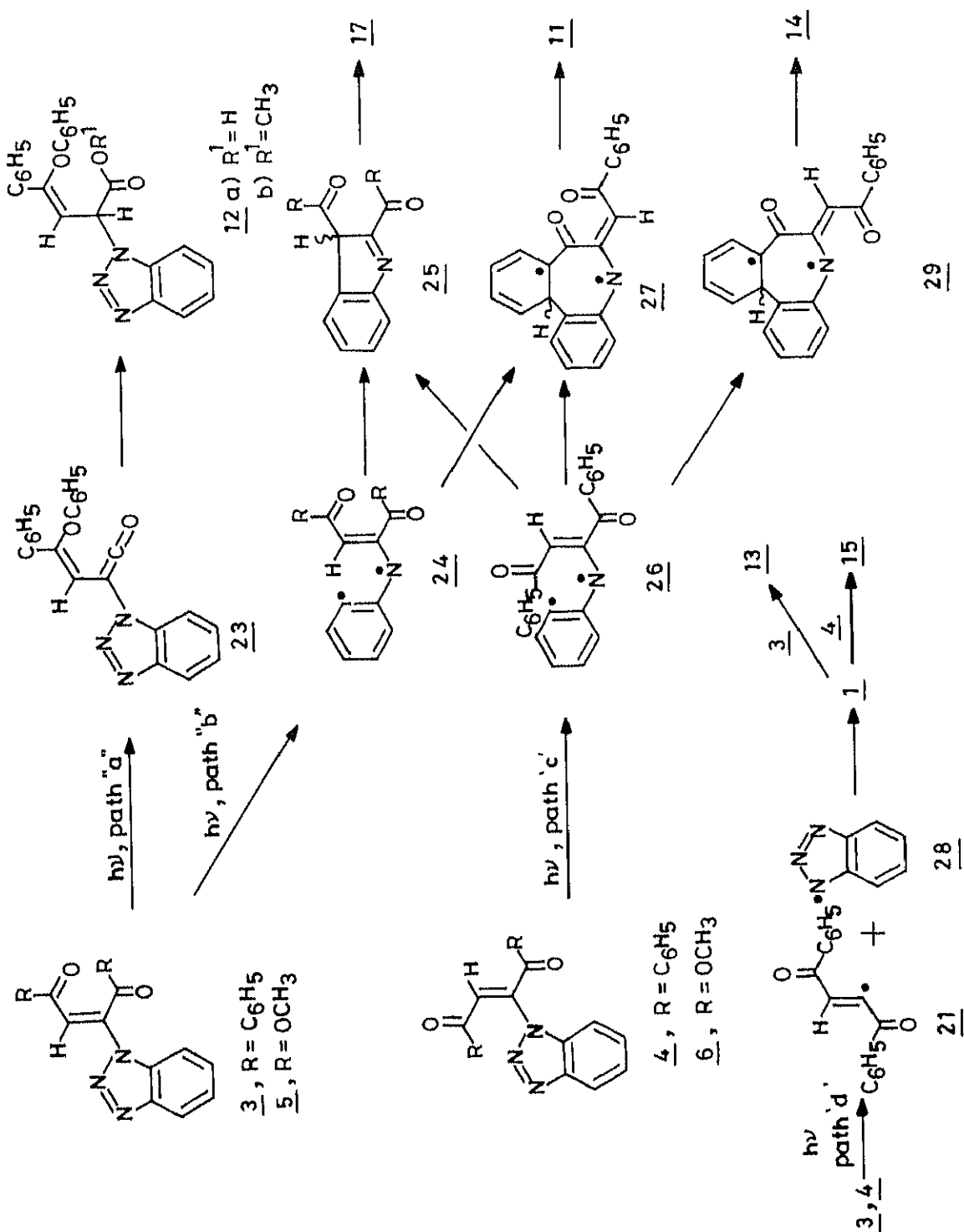


Figure III.7 ^1H NMR spectrum (90 MHz) of **19b**.

triazolyl-1,2-dibenzoylalkenes (3, 4, 8 and 9) under discussion. One of these, involves the 1,2-dibenzoylalkene rearrangement,¹² leading to ketene derived products 12a and 12b (path "a" in Scheme III.5), observed in the cases of 3 and 4. Another type of photoreaction, observed in the cases of 3 and 4, leads to the formation of the benzazepinone derivatives 11 and 14, respectively. In this case, the primary step involves the photochemical loss of nitrogen from the benzotriazolyl moiety, leading to biradical intermediates 24 and 26, which can subsequently cyclize to give 27 and 29, and ultimately the benzazepinones 11 and 14, respectively (path "b" and "c", Scheme III.5). Mention may be made in this connection, that several examples of photoelimination of nitrogen from benzotriazoles, leading to biradical intermediates are reported in the literature.¹³ The third type of photoreaction observed in the cases of 3 and 4, involves a photofragmentation reaction leading to radical intermediates 21 and 28, which can ultimately lead to the triazole 1 and the dibenzoylethylene 22a, respectively (path "d", Scheme III.5). The formation of the butanediones 13 and 15, however, may be explained in terms of the addition of the triazole 1 to the starting 1,2-dibenzoylalkenes 3 and 5, respectively. In the case of the triazolyl-1,2-dibenzoylalkenes 9 and 8, the major pathway involves the formation of the dihydrotriazoloisoquinoline derivatives 19a and 19b, respectively, through a 10 or 14 electron photochemical electrocyclic ring closure reaction and involving zwitterionic intermediates such as 18, as shown in Scheme III.4.



The formation of trans-1,2-dibenzoylethylene (22a) and the triazole 7 in these reactions may proceed through a photofragmentation of 9 and 8 to give radical intermediates such as 20 and 21, which could then lead to the observed products. The formation of trans-1,2-dibenzoylmethoxyethylene (22b) in the reaction of 9 in methanol, however, may proceed through an addition elimination mechanism.^{6,9} It is interesting to note that in the cases of the triazolylmaleate 5 and the fumarate 6, the major photochemical pathway proceeds primarily through the loss of nitrogen, leading to the diradical intermediate 24, which can combine with benzene (solvent) to give the insertion product 16 or undergo ring closure reaction, leading to the indole derivative 17 (Scheme III.3). In addition, a minor process observed, in case of the benzotriazolyl maleate 5, involves a cis-trans photoisomerization leading to the fumarate 6.

III.3.4 Laser Flash Photolysis Studies.¹⁴ Employing nanosecond pulse excitation (308 or 337.1 nm), the time-resolved aspects of the photochemistry of the substrates in question were briefly explored in terms of transient absorbance changes over 0.1-100 μ s. Upon 308 nm laser excitation, neither the maleate 5 nor the fumarate 6 in deaerated benzene solutions showed any transient or permanent absorbance changes at 315-700 nm that could be ascribed to the formation of biradicals 24 and 26 or cis-trans photoisomerization. This, however, should not be considered contradictory to the results of

preparative photochemistry, because the quantum yield of these phototransformations from 5 and 6 are possibly low and/or the extinction coefficients of related transients can be small.

The 308 or 337.1 nm laser flash photolysis of cis-dibenzoylalkene 3 in a benzene solution results in negative absorbance changes in the spectral region of its lowest-energy absorption band system (320-380 nm), see Figure III.8, part A. At short wavelengths (300-310 nm), small positive absorbance changes are observed. On our longest time scale (100 μ s), the ground state bleaching and the positive absorption at short wavelengths do not show any sign of recovery or decay. Air saturation ($[O_2] \sim 2$ mM) does not affect the yields and decay characteristics of the observed absorbance changes. On going from benzene to methanol as solvent, under both deaeration and air-saturation, growths of long-lived absorption are observed at 345-400 nm (in addition to the bleaching at shorter wavelengths), see Figure III.8, part B. The growth process occurs with first-order kinetics ($\tau = 11 \mu$ s), independent of oxygen concentration in the solution. Also, the plateau absorbance at the completion of the growth process remains essentially unchanged in the absence or presence of oxygen (≤ 2 mM).

That the growth process is related to the reaction of a photointermediate with a hydroxylic reagent is shown by the fact that similar transient phenomena are also observed in benzene-methanol, methanol-water and acetonitrile-water mixtures. In the latter, a linear dependence of the rate constant (k_{obsd})

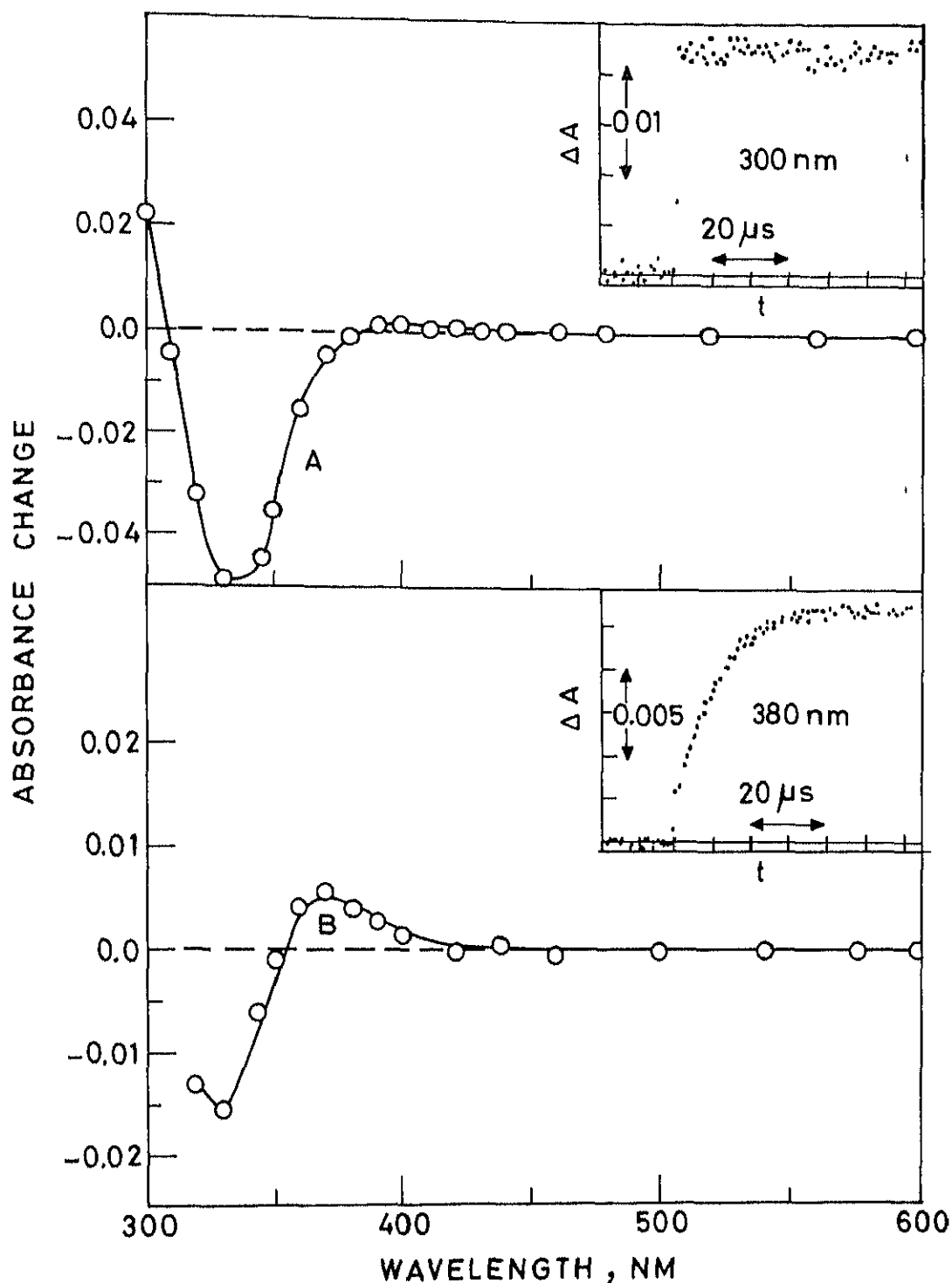
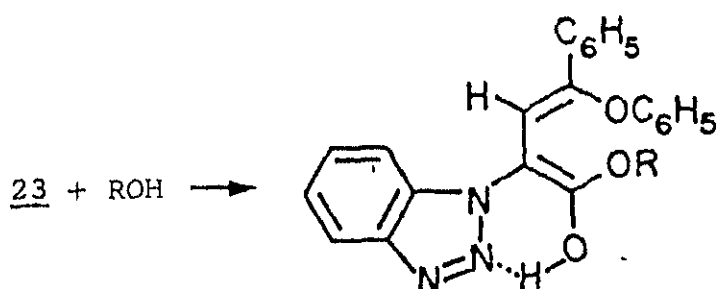


Figure III.8 Absorbance changes observed at (A) 6 μ s and (B) 60 μ s following 337.1 nm laser excitation of (A) 0.25 mM 3 in benzene and (B) 0.13 mM 3 in methanol. Insets: representative kinetic traces for 3 at (a) 300 nm in benzene and (b) 380 nm in methanol.

for the growth process on water concentration is noted; from the plot of k_{obsd} against $[\text{H}_2\text{O}]$, a value of $5 \times 10^4 \text{ M}^{-1}\text{s}^{-1}$ is obtained for the reaction of the photointermediate in question with H_2O in acetonitrile.

In view of the fact that under steady-state irradiation of 3 in methanol the predominant photoreaction is the intramolecular phenyl group migration leading to the ketene 23 which subsequently reacts with methanol, it seems possible that the growth process observed in the presence of hydroxylic reagents is due to the transformation of 23 to an enol (shown below) or



enolate anion. Similar results have been obtained earlier for 1-pyrazolyl-cis-1,2-dibenzoylalkene systems for which the 1,2-dibenzoylalkene rearrangement has been shown^{6,9} to be particularly facile.

The 337.1 nm laser flash photolysis of 8 in benzene results in weak absorbance changes due to a short-lived transient species ($\tau = 360 \text{ ns}$) which absorbs at 450-650 nm ($\lambda_{\text{max}} = 550 \text{ nm}$, Figure III.9, Parts A and B). Following the decay of this species, a longer-lived, weak component ($\tau = 14 \mu\text{s}$) absorbing at 410-550 nm is observed. The decay of the short-

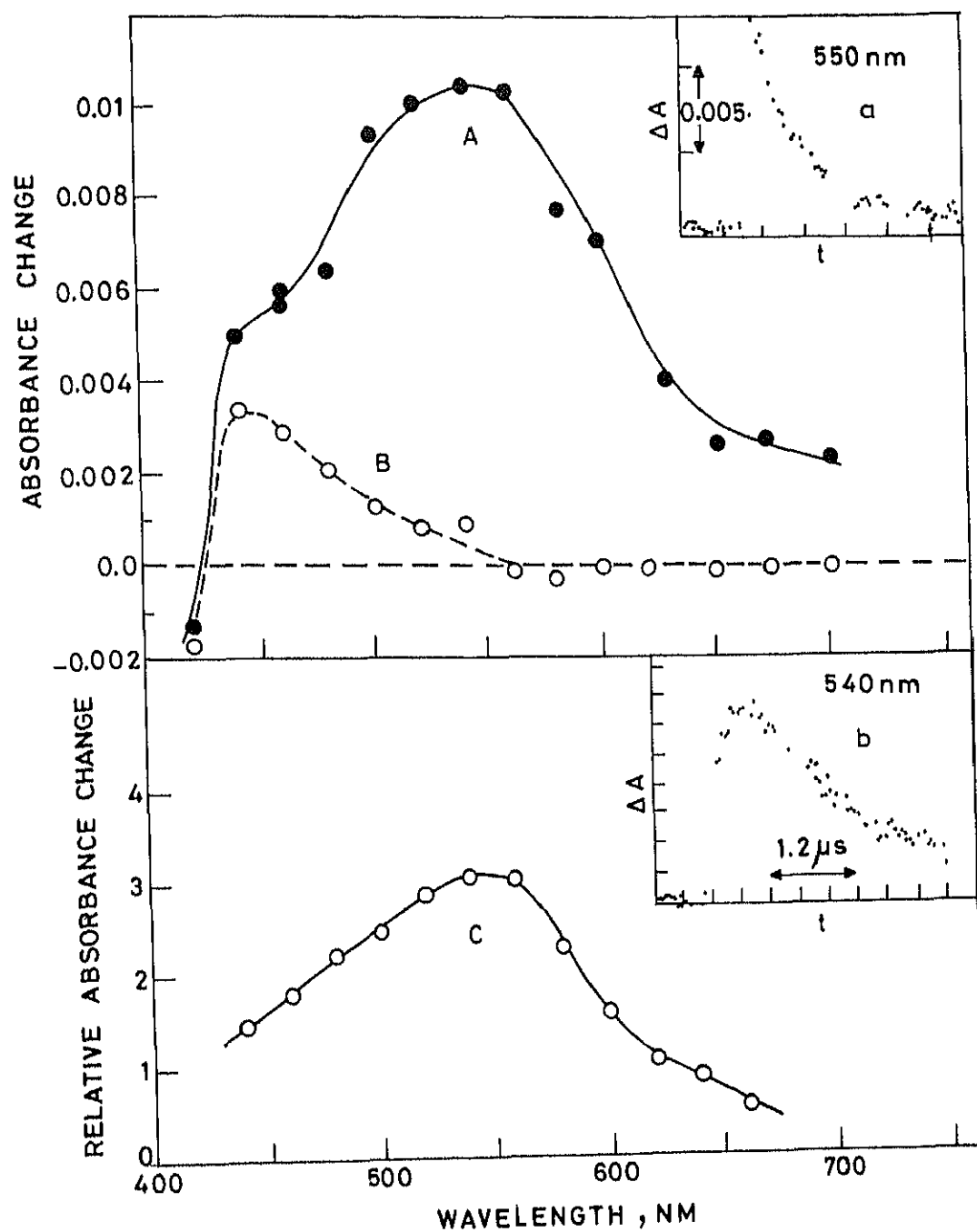


Figure III.9 Transient absorption spectra at (A) 0.5 μ s and (B) 2.5 μ s following 337.1 nm laser flash photolysis of 0.45 mM 8 in benzene and (C) at 0.8 μ s following pulse radiolysis of 0.05 M biphenyl in the presence of 0.8 mM 8 in benzene. Insets: representative kinetic traces for 8 in benzene at (a) 550 nm upon 337.1 nm laser flash excitation and (b) 540 nm upon electron pulse irradiation in the presence of biphenyl.

lived species becomes enhanced in the presence of oxygen ($k_q = 1.9 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$) and ferrocene ($k_q = 3.5 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$), but remains unaffected upon adding trans-piperylene up to 0.3 M. This quenching behaviour strongly suggests that the species observed is the triplet of 8. This is confirmed by the fact that upon pulse radiolysis of biphenyl (0.05 M) in the presence of 0.5-5.0 mM of 8 in benzene, a delayed formation of the 550 nm species is seen as a result of triplet sensitization by pulse-radiolytic biphenyl triplet.^{6,9} This is illustrated in Figure III.9, part C. The transient nature and oxygen insensitivity of the longer-lived component (400-550 nm) suggest that this can possibly be the switterion 18 leading to the dihydro-triazoloisoquinoline derivative 19 (the major product isolated in steady-state photolysis). In methanol solution, the lifetime of the short-lived species derived from 8 becomes shortened ($\tau = 140 \text{ ns}$). No growth or long-lived absorption similar to that seen in the case of 3 is noticed in the case of 8 in methanol; this is compatible with the lack of observation of intramolecular phenyl group migration in the course of the steady-state irradiation of 8.

III.4 EXPERIMENTAL SECTION

All melting points are uncorrected and were determined on a Mel-Temp melting point apparatus. The IR spectra were recorded on Perkin-Elmer Model 377 or Model 580 infrared spectrophotometers. The electronic spectra were recorded on

Cary 17D or Cary 219 spectrophotometers. The ^1H NMR traces were recorded on Varian EM-390 or HA-100 NMR spectrometers, whereas ^{13}C NMR spectra were recorded on either Bruker CFT-80 or Bruker 400 NMR spectrometers using tetramethylsilane as internal standard. The mass spectra were recorded on a Hitachi RMU-GE single-focussing mass spectrometer or a Varian Mat CH7 mass spectrometer at 70 eV. Irradiations were carried out in a Srinivasan-Griffin-Rayonet photochemical reactor (RPR, 2537 Å or 3000 Å) using a quartz vessel.

III.4.1 Starting Materials. 1,2,3-Benzotriazole (1),¹⁵ mp 96-97 °C, 3,5-diphenyl-1H-1,2,4-triazole (7),¹⁶ mp 188-189 °C, DBA (2a),^{17,18} mp 110-111 °C, and DMAD (2b),¹⁹ bp 95-98 °C (10 mm) were prepared by reported procedures. Solvents for steady-state photolysis were purified and distilled before use, whereas Aldrich Gold label solvents were used for laser studies. Petroleum ether used was the fraction with bp 60-80 °C.

III.4.2 Preparation of the Starting Materials 3-6.

A general procedure was to add a benzene solution of the benzotriazole 1 (10 mmol, in 25 mL) to a stirred solution of the acetylenic compound (2a or 2b, 10 mmol) in benzene (25 mL) at room temperature (~28 °C) over 0.5 h and the stirring was continued for an additional period of 24 h. Removal of the solvent under vacuum gave a residual solid, which was chromatographed over silica gel. Elution with a mixture (1:4) of benzene and

petroleum ether gave the Z isomer first and further elution with a mixture (1:3) of benzene and petroleum ether gave the E isomer. These adducts were purified by recrystallization from a mixture (1:1) of benzene and petroleum ether, in each case.

(E)-1-(1,2,3-Benzotriazolyl)-1,2-dibenzoylethylene (3).

3 was obtained in a 51% yield, mp 181 °C.

IR spectrum ν_{\max} (KBr): 3090, 3075, and 3045 (ν_{CH}), 1675 and 1655 ($\nu_{\text{C=O}}$), 1605 and 1585 ($\nu_{\text{C=C}}$ and $\nu_{\text{N=N}}$) cm^{-1} .

UV spectrum λ_{\max} (methanol): 217 nm (ϵ , 9,750), 255 (14,800), and 319 (2,870).

^1H NMR spectrum (CDCl_3): δ 6.28 (s, 1 H, vinylic), and 7.20-8.25 (m, 14 H, aromatic).

^{13}C NMR spectrum (CDCl_3): δ 111.49, 120.86, 125.31, 128.49, 128.61, 128.73, 128.83, 128.90, 128.97, 129.57, 129.88, 131.20, 133.66, 134.07, 135.67, 145.59, 189.21 and 191.16.

Mass spectrum m/e (relative intensity): 353 (M^+ , 1), 325 ($\text{M}^+ - \text{N}_2$, 2), 297 (3), 276 ($\text{M}^+ - \text{C}_6\text{H}_5$, 8), 248 ($\text{M}^+ - \text{COC}_6\text{H}_5$, 30), 220 ($\text{M}^+ - \text{COC}_6\text{H}_5 - \text{N}_2$, 48), 105 ($\text{C}_6\text{H}_5\text{CO}^+$, 100), and other peaks.

Anal. Calcd for $\text{C}_{22}\text{H}_{15}\text{N}_3\text{O}_2$: C, 74.79; H, 4.25; N, 11.90. Found: C, 74.58; H, 4.33; N, 11.73.

(Z)-1-(1,2,3-Benzotriazolyl)-1,2-dibenzoylethylene (4).

4 was obtained in a 33% yield, mp 171 °C.

IR spectrum ν_{\max} (KBr): 3085, 3070, and 3050 (ν_{CH}), 1675 and 1655 ($\nu_{\text{C=O}}$), 1610 and 1595 ($\nu_{\text{C=C}}$ and $\nu_{\text{C=N}}$) cm^{-1} .

UV spectrum λ_{\max} (Methanol): 217 nm (ϵ , 10,500), 258 (17,380), and 325 (3,900).

^1H NMR spectrum (CDCl_3): δ 7.05-8.30 (m, aromatic and vinylic).

^{13}C NMR spectrum (CDCl_3): δ 114.01, 120.92, 125.35, 128.57, 128.62, 128.66, 128.73, 128.84, 128.88, 128.97, 129.57, 131.35, 133.83, 135.39, 136.91, 146.70, 190.03, and 193.11.

Mass spectrum, m/e (relative intensity): 353 (M^+ , 1), 325 ($\text{M}^+ - \text{N}_2$, 2), 297 (4), 276 (9), 248 (34), 220 ($\text{M}^+ - \text{COC}_6\text{H}_5$, $-\text{N}_2$, 44), 105 ($\text{C}_6\text{H}_5\text{CO}^+$, 100), and other peaks.

Anal. Calcd for $\text{C}_{22}\text{H}_{15}\text{N}_3\text{O}_2$: C, 74.79; H, 4.29; N, 11.90. Found: C, 74.62; H, 4.41; N, 11.69.

Dimethyl 1-Benzotriazolylmaleate (5). 5 was obtained in 56% yield, mp 97-98 °C.

IR spectrum ν_{\max} (KBr): 3090, 3070, 3049, 3023, 3008, 2949, and 2836 (ν_{CH}), 1730 and 1716 ($\nu_{\text{C=O}}$), 1645 and 1600 ($\nu_{\text{C=C}}$ and $\nu_{\text{N=N}}$) cm^{-1} .

UV spectrum λ_{\max} (methanol): 219 nm (ϵ , 7,280), 256 (9,250), and 282 (5,830).

^1H NMR spectrum (CDCl_3): δ 3.55 (s, 3 H, methoxy), 3.90 (s, 3 H, methoxy), and 7.10-8.25 (m, 5 H, aromatic and vinylic).

^{13}C NMR spectrum (CDCl_3): δ 51.77, 53.04, 109.81, 119.42, 123.81, 127.89, 127.98, 133.07, 133.43, 144.95, 161.45, and 162.20.

Mass spectrum, m/e (relative intensity): 261 (M^+ , 83), 230 ($\text{M}^+ - \text{OCH}_3$, 11), 202 ($\text{M}^+ - \text{CO}_2\text{CH}_3$, 54), 201 (7), 199 ($\text{M}^+ - 2\text{OCH}_3$, 11), 188 ($\text{M}^+ - \text{CO}_2\text{CH}_3$, $-\text{CH}_2$, 21), 187 (24), 174 ($\text{M}^+ - \text{CO}_2\text{CH}_3$, $-\text{N}_2$, 51), 160 ($\text{M}^+ - \text{CO}_2\text{CH}_3$, $-\text{CH}_2$, $-\text{N}_2$, 42), 159 ($\text{M}^+ - \text{CO}_2\text{CH}_3$, $-\text{CH}_3$, $-\text{N}_2$, 60), 59 (CO_2CH_3^+ , 100), and other peaks.

Anal. Calcd for $\text{C}_{12}\text{H}_{11}\text{N}_3\text{O}_4$: C, 55.17; H, 4.21; N, 16.09. Found: C, 55.33; H, 4.16; N, 16.27.

Dimethyl 1-Benzotriazolylfumarate (6). 6 was obtained in 38% yield, mp 90-91 $^\circ\text{C}$.

IR spectrum ν_{max} (KBr): 3090, 3000, 2947, and 2839 (ν_{CH}), 1745 and 1710 ($\nu_{\text{C=O}}$), 1633 and 1600 ($\nu_{\text{C=C}}$ and $\nu_{\text{N=N}}$) cm^{-1} .

UV spectrum λ_{max} (methanol): 219 nm (ϵ , 7,280), 256 (9,750), and 309 (5,530).

^1H NMR spectrum (CDCl_3): δ 3.95 (s, 3 H, methoxy), 4.10 (s, 3 H, methoxy), and 6.75-8.20 (m, 5 H, aromatic and vinylic).

^{13}C NMR spectrum (CDCl_3): δ 51.99, 53.18, 109.79, 110.81, 120.51, 125.12, 129.30, 130.78, 139.78, 146.18, 161.81, and 164.06.

Mass spectrum, m/e (relative intensity): 261 (M^+ , 82), 230 (10), 202 ($M^+ - CO_2CH_3$, 45), 199 (12), 188 (16), 187 (13), 174 ($M^+ - CO_2CH_3$, $-N_2$, 55), 160 (45), 159 (77), 59 ($CO_2CH_3^+$, 100), and other peaks.

Anal. Calcd for $C_{12}H_{11}N_3O_4$: C, 55.17; H, 4.21; N, 16.09. Found: C, 54.98; H, 4.31; N, 16.18.

III.4.3 Reaction of 3,5-Diphenyl-1H-1,2,4-triazole (7) with DBA (2a). In Benzene. A mixture of 7 (2.21 g, 10 mmol) and DBA (2a, 2.34 g, 10 mmol) in benzene (50 mL) was stirred at room temperature for 48 h and the solvent was removed under vacuum to give a residual solid, which was chromatographed over silica gel. Elution with a mixture (1:2) of benzene and petroleum ether gave 0.55 g (12%) of (8)-1-(3,5-diphenyl-1H-1,2,4-triazolyl)-1,2-dibenzoyl ethylene (9), mp 154-155 °C, after recrystallization from methanol.

IR spectrum ν_{max} (KBr): 3093, 3075, and 3045 (ν_{CH}), 1665 and 1650 ($\nu_{C=O}$), 1612 and 1600 ($\nu_{C=C}$), 1485 ($\nu_{C=N}$) cm^{-1} .

UV spectrum λ_{max} (methanol): 215 nm (ϵ , 34,780), and 256 (48,540).

1H NMR spectrum ($CDCl_3$): δ 6.95-8.60 (m, aromatic and vinylic).

Mass spectrum, m/e (relative intensity): 455 (M^+ , 10), 378 ($M^+ - C_6H_5$, 3), 352 ($M^+ - C_6H_5CN$, 43), 351 (8), 350 ($M^+ - COC_6H_5$, 84), 275 ($M^+ - C_6H_5CN$, $-C_6H_5$, 9), 105 ($C_6H_5CO^+$, 100),

103 (59) and other peaks).

Anal. Calcd for $C_{30}H_{21}N_3O_2$: C, 79.12; H, 4.62; N, 9.26.
Found: C, 79.35; H, 4.72; N, 9.39.

Further elution of the column with a mixture (1:1) of benzene and petroleum ether gave 2.8 g (61%) of (E)-1-(3,5-diphenyl-1H-1,2,4-triazolyl)-1,2-dibenzoyl-ethylene (8), mp 190-191 °C, after recrystallization from methanol.

IR spectrum ν_{\max} (KBr): 3094, 3075, and 3040 (ν_{CH}), 1660 and 1640 ($\nu_{C=O}$), 1610 and 1595 ($\nu_{C=C}$ and $\nu_{C=N}$) cm^{-1} .

UV spectrum λ_{\max} (methanol): 216 nm (ϵ , 31,450) and 246 (38,750).

1H NMR spectrum ($CDCl_3$): δ 6.75 (s, 1 H, vinylic), and 7.10-8.60 (m, 20 H, aromatic).

Anal. Calcd for $C_{30}H_{21}N_3O_2$: C, 79.12; H, 4.62; N, 9.26.
Found: C, 78.93; H, 4.49; N, 9.38.

In a repeat experiment, a mixture of 7 (2.21 g, 10 mmol) and DBA (2.34 g, 10 mmol) in acetonitrile (40 mL) was refluxed for 24 h and worked up by removal of the solvent under vacuum and chromatographing the residue over silica gel. Elution with a mixture (1:2) of benzene and petroleum ether gave 1.6 g (36%) of Z-1-(3,5-diphenyl-4H-1,2,4-triazolyl)-1,2-dibenzoyl-ethylene (10), mp 156-157 °C, after recrystallization from methanol.

IR spectrum ν_{\max} (KBr): 3090, 3075, and 3042 (ν_{CH}), 1662 and 1648 ($\nu_{\text{C=O}}$), 1610 and 1595 ($\nu_{\text{C=C}}$) and 1585 ($\nu_{\text{C=N}}$) cm^{-1} .

UV spectrum λ_{\max} (methanol): 215 nm (ϵ , 37,280), and 247 (49,380).

^1H NMR spectrum (CDCl_3): δ 7.05–8.55 (m, aromatic and vinylic).

Mass spectrum, m/e (relative intensity): 455 (M^+ , 73), 427 ($\text{M}^+ - \text{N}_2$, 78), 350 ($\text{M}^+ - \text{COC}_6\text{H}_5$, 91), 349 (12), 322 ($\text{M}^+ - \text{COC}_6\text{H}_5$, $-\text{N}_2$, 21), 245 (26), 105 ($\text{C}_6\text{H}_5\text{CO}^+$, 100), and other peaks.

Anal. Calcd for $\text{C}_{30}\text{H}_{21}\text{N}_3\text{O}_2$: C, 79.16; H, 4.62; N, 9.23.
Found: C, 78.96; H, 4.51; N, 9.37.

Further elution of the column with a mixture (1:1) of benzene and petroleum ether gave 1.9 g (41%) of 9, mp 156 °C (mixture melting point), after recrystallization from methanol.

III.4.4 Irradiation of (E)-Benzotriazolyl-1,2-dibenzoyl-ethylene (3). A In Benzene. A solution of 3 (500 mg, 1.45 mmol) in benzene (500 mL) was deaerated by purging with nitrogen and irradiated (RPR, 3000 Å) for 4.5 h. The solvent was removed under vacuum and the residual solid was chromatographed over silica gel. Elution of the column with a mixture (1:9) of benzene and petroleum ether gave 55 mg (12%) of the benzazepinone 11, mp 167–168 °C, after recrystallization from a mixture (1:1) of methylene chloride and methanol.

IR spectrum ν_{\max} (KBr): 3345 (ν_{NH}), 3083, 3055, and 3030 (ν_{CH}), 1715 and 1645 ($\nu_{\text{C=O}}$), 1600 and 1586 ($\nu_{\text{C=C}}$) cm^{-1} .

UV spectrum λ_{\max} (methanol): 222 nm (ϵ , 5,180), and 310 (8,160).

^{13}C NMR spectrum (CDCl_3): δ 119.54, 120.31, 122.63, 124.51, 125.21, 126.73, 126.98, 128.54, 128.77, 129.36, 129.78, 131.32, 133.47, 133.79, 134.21, 150.36, 153.59, 193.23 (C=O), and 198.78 (C=O).

Mass spectrum, m/e (relative intensity): 325 (M^+ , 20), 324 ($\text{M}^+ - \text{H}$, 100), 296 ($\text{M}^+ - \text{CO}$, $-\text{H}$, 13), 295 ($\text{M}^+ - \text{CO}$, -2 H , 48), 247 ($\text{M}^+ - \text{C}_6\text{H}_5$, $-\text{H}$, 12), 220 ($\text{M}^+ - \text{COC}_6\text{H}_5$, 18), 180 ($\text{C}_{13}\text{H}_8\text{O}^+$, 11), 167 ($\text{C}_{12}\text{H}_9\text{N}^+$, 17), 166 (21), 105 ($\text{C}_6\text{H}_5\text{CO}^+$, 33), and other peaks.

Anal. Calcd for $\text{C}_{22}\text{H}_{15}\text{NO}_2$: C, 81.23; H, 4.62; N, 4.31.
Found: C, 81.46; H, 4.39; N, 4.52.

Further elution of the column with a mixture (1:2) of benzene and petroleum ether gave 100 mg (20%) of the unchanged starting material 3, mp 179-180 $^{\circ}\text{C}$ (mixture melting point), after recrystallization from methanol.

Subsequent elution with a mixture (1:1) of benzene and petroleum ether gave 250 mg (38%) of meso-2,3-bisbenzotriazolyl-1,4-diphenylbutane-1,4-dione (13), mp 192-193 $^{\circ}\text{C}$, after recrystallization from a mixture (1:1) of methylene chloride and petroleum ether.

IR spectrum ν_{\max} (KBr): 3085, 3062, 3020, 2971, 2860, and 2852 (ν_{CH}), 1688 ($\nu_{\text{C=O}}$), 1610 and 1592 ($\nu_{\text{C=C}}$ and $\nu_{\text{C=N}}$) cm^{-1} .

UV spectrum λ_{\max} (methanol): 218 nm (ϵ , 11,900), 258 (25,960), and 327 (1,590).

^{13}NMR spectrum (CDCl_3): δ 61.64, 120.26, 124.37, 128.52, 128.89, 129.03, 132.24, 134.05, 135.13, 135.84, 145.73, and 190.75 (C=O).

Mass spectrum, m/e (relative intensity): 367 ($\text{M}^+ - \text{COC}_6\text{H}_5$, 35), 354 ($\text{M}^+ - \text{C}_6\text{H}_4\text{N}_3$, 6), 353 ($\text{M}^+ - \text{C}_6\text{H}_4\text{N}_3$, -H, 11), 325 ($\text{M}^+ - \text{C}_6\text{H}_4\text{N}_3$, -H, -N₂, 10), 324 ($\text{M}^+ - \text{C}_6\text{H}_4\text{N}_3$, -2 H, -N₂, 12), 297 ($\text{M}^+ - \text{C}_6\text{H}_4\text{N}_3$, -H, -N₂, -CO, 22), 296 ($\text{M}^+ - \text{C}_6\text{H}_4\text{N}_3$, -2 H, -N₂, -CO, 48), 280 (15), 268 (14), 248 (15), 220 (56), 219 (36), 105 ($\text{C}_6\text{H}_5\text{CO}^+$, 100), and other peaks.

Anal. Calcd for $\text{C}_{28}\text{H}_{20}\text{N}_6\text{O}_2$: C, 71.18; H, 4.27; N, 17.78. Found: C, 71.32; H, 4.15; N, 17.61.

Final elution of the column with benzene gave 55 mg (10%) of 2-(1-(1,2,3-benzotriazolyl)-4-phenoxy-4-phenyl-3-butenic acid (12a), mp 261-262 °C, after recrystallization from a mixture (2:1) of methylene chloride and petroleum ether.

IR spectrum ν_{\max} (KBr): 3085, 3055, and 3025 (ν_{CH}), 3000-2500 (ν_{OH} , carboxylic), 1740 ($\nu_{\text{C=O}}$), 1650, 1610 and 1595 ($\nu_{\text{C=C}}$ and $\nu_{\text{N=N}}$) cm^{-1} .

UV spectrum λ_{\max} (methanol): 218 nm (ϵ , 5,530), and 258 (19,730).

^1H NMR spectrum (CDCl_3): δ 5.75 (d, $J = 8.8$ Hz, 1 H, methine), 6.34 (d, $J = 8.8$ Hz, 1 H, vinylic), 6.95-8.15 (m, 14 H, aromatic), and 8.30 (s, 1 H, D_2O -exchangeable, OH).

Anal. Calcd for $\text{C}_{22}\text{H}_{17}\text{N}_3\text{O}_3$: C, 71.16; H, 4.58; N, 11.32. Found: C, 71.34; H, 4.67; N, 11.08.

B In Methanol. Irradiation of 3 (500 mg, 1.415 mmol) in methanol (500 mL) for 4.5 h (RPR, 3000 Å) and removal of the solvent under vacuum gave a residual solid which was chromatographed on silica gel. Elution with a mixture (1:4) of benzene and petroleum ether gave 340 mg (62%) of methyl 2-(1-(1,2,3-benzotriazolyl))-4-phenoxy-4-phenyl-3-butenate (12b), mp 143-144 °C, after recrystallization from a mixture (1:1) of benzene and cyclohexane.

IR spectrum ν_{max} (KBr): 3085, 3065, 3022, 2994, 2969, 2886, and 2848 (ν_{CH}), 1748 ($\nu_{\text{C=O}}$), 1645, 1618, and 1600 ($\nu_{\text{C=C}}$ and $\nu_{\text{N=N}}$) cm^{-1} .

UV spectrum λ_{max} (methanol): 218 nm (ϵ , 6,260), and 250 (4,970).

^1H NMR spectrum (CDCl_3): δ 3.65 (s, 3 H, methoxy), 5.80 (d, $J = 9$ Hz, 1 H, methine), 6.20 (d, $J = 9$ Hz, 1 H, vinylic), and 7.00-8.10 (m, 14 H, aromatic).

Mass spectrum, m/e (relative intensity): 326 ($\text{M}^+ - \text{CO}_2\text{CH}_3$, 11), 299 (11), 298 ($\text{M}^+ - \text{CO}_2\text{CH}_3$, $-\text{N}_2$, 46), 293 (20), 292 ($\text{M}^+ - \text{OC}_6\text{H}_5$, 100), 267 ($\text{M}^+ - \text{C}_6\text{H}_4\text{N}_3$, 8), 233 (5), 220 (6), 208 (15),

207 (M^+ $-C_6H_4N_3$, $-CO_2CH_3$, $-H$, 59), 206 (5), 205 (M^+ $-OC_6H_5$, $-CO_2CH_3$, $-N_2$, 14), 204 (M^+ $-OC_6H_5$, $-CO_2CH_3$, $-N_2$, $-H$, 26), and other peaks.

Subsequent elution of the column with a mixture (1:2) of benzene and petroleum ether gave 60 mg (12%) of the unchanged starting material 3, mp 179-180 °C (mixture melting point), after recrystallization from (1:1) methylene chloride and petroleum ether.

Further elution of the column with a mixture (1:1) of benzene and petroleum ether gave 25 mg (4%) of the bisbenzotriazolylbutanedione 13, mp 192-193 °C (mixture melting point), after recrystallization from a mixture (1:1) of methylene chloride and petroleum ether.

III.4.5 Irradiation of (Z)-1-(1,2,3-Benzotriazolyl)-1,2-dibenzoyl ethylene (4). A In Benzene. A solution of 4 (500 mg, 1.415 mmol) in benzene (500 mL) was irradiated (RPR, 3000 Å) for 4.5 h. Removal of the solvent under vacuum gave a residual solid which was chromatographed over silica gel. Elution with a mixture (1:4) of benzene and petroleum ether gave 50 mg (11%) of the benzazepinone 14, mp 177 °C, after recrystallization from a mixture (1:1) of methylene chloride and methanol.

IR spectrum ν_{max} (KBr): 3380-3300 (ν_{NH}), 3080, 3050, and 3028 (ν_{CH}), 1718 and 1645 ($\nu_{C=O}$), 1600 and 1586 ($\nu_{C=C}$) cm^{-1} .

UV spectrum λ_{\max} (methanol): 222 nm (ϵ , 5380), and 316 (8,600).

Mass spectrum, m/e (relative intensity): 325 (M^+ , 25), 324 ($M^+ - H$, 100), 296 ($M^+ - H$, $-CO$, 15), 295 ($M^+ - 2H$, $-CO$, 50), 247 ($M^+ - C_6H_5$, $-H$, 10), 220 ($M^+ - COC_6H_5$, 47), 180 ($C_{13}H_8O^+$, 15), 167 ($C_{12}H_7N^+$, 20), 166 (19), 105 ($C_6H_5CO^+$, 26), and other peaks.

Anal. Calcd for $C_{22}H_{15}NO_2$: C, 81.23; H, 4.62; N, 4.31.

Found: C, 81.42; H, 4.51; N, 4.23.

Further elution of the column with a mixture (1:2) of benzene and petroleum ether gave 30 mg (6%) of the E isomer 3, mp 179-180 °C (mixture melting point), after recrystallization from a mixture (1:1) of methylene chloride and petroleum ether.

Subsequent elution of the column with a mixture (1:2) of benzene and petroleum ether gave 240 mg (36%) of d,l-2,3-bis-(1-(1,2,3-benzotriazolyl))-1,4-diphenylbutane-1,4-dione (15), mp 182-183 °C, after recrystallization from a mixture (1:1) of methylene chloride and petroleum ether.

IR spectrum ν_{\max} (KBr): 3080, 3060, 3020, 2970, 2915, 2860 and 2850 (ν_{CH}), 1663 ($\nu_{C=O}$), 1610 and 1592 ($\nu_{C=C}$ and $\nu_{N=N}$) cm^{-1} .

UV spectrum λ_{\max} (Methanol): 215 nm (ϵ , 5,880), 252 (11,240), and 326 (1,910).

Mass spectrum, m/e (relative intensity): 354 ($M^+ - C_6H_4N_3$, 5), 353 ($M^+ - C_6H_4N_3$, $-H$, 10), 325 ($M^+ - C_6H_4N_3$, $-H$, $-N_2$, 15),

324 ($M^+ - C_6H_4N_3$, -2 H, $-N_2$, 10), 297 ($M^+ - C_6H_4N_3$, -H, $-N_2$, -CO, 20), 296 ($M^+ - C_6H_4N_3$, -2 H, $-N_2$, -CO, 45), 280 (10), 268 (20), 248 (15), 220 (55), 219 (35), 105 ($C_6H_5CO^+$, 100), and other peaks.

Anal. Calcd For $C_{28}H_{20}N_6O_2$: C, 71.18; H, 4.27; N, 17.78.
Found: C, 71.40; H, 4.38; N, 17.93.

Further elution of the column with benzene gave 30 mg (6%) of the acid 12a, mp 261-262 °C (mixture melting point), after recrystallization from a mixture (2:1) of methylene chloride and petroleum ether.

B In Methanol. In a repeat experiment, a solution of 4 (500 mg, 1.415 mmol) in methanol (500 mL) was irradiated (RPR, 3000 Å) for 4.5 h and worked up by a similar procedure to give 290 mg (53%) of 12b, mp 143-144 °C (mixture melting point), after recrystallization from a mixture (1:1) of benzene and cyclohexane, 70 mg (14%) of the unchanged starting material 4, mp 170-171 °C (mixture melting point), after recrystallization from a mixture (1:1) of methylene chloride and petroleum ether and 40 mg (6%) of 15, mp 182-183 °C (mixture melting point), after recrystallization from methanol.

III.4.6 Conversion of 12a to 12b. To a solution of 12a (55 mg, 0.2 mmol) in ether (5 mL) was added an ether solution of diazomethane (1 mL, 5%) at 0 °C, with stirring and the stirring was continued for an additional period of 1.5 h. Removal

of the solvent under vacuum gave a residual solid, which was recrystallized from a mixture (1:1) of benzene and cyclohexane to give 40 mg (76%) of the ester 12b, mp 144 °C (mixture melting point).

III.4.7 Thermal Transformation of 11 to 14. A solution of 11 (40 mg, 0.12 mmol) in methanol (20 mL) was refluxed for 3 h. Removal of the solvent under vacuum gave a residual solid, which was chromatographed over silica gel. Elution with petroleum ether gave 25 mg (63%) of 14, mp 177 °C (mixture melting point), after recrystallization from a mixture (1:1) of methylene chloride and petroleum ether. Further elution of the column with a mixture (1:9) of benzene and petroleum ether gave 8 mg (20%) of the unchanged starting material 11, mp 169 °C (mixture melting point), after recrystallization from a mixture (1:1) of methylene chloride and methanol.

III.4.8 Base-catalyzed Transformation of 11 to 14. A mixture of 11 (20 mg, 0.06 mmol) and triethylamine (100 mg, 1.0 mmol) in benzene (10 mL) was stirred at room temperature for 1 h. Removal of the solvent under vacuum and recrystallization of the residue from a mixture (1:1) of methylene chloride and methanol gave 18 mg (90%) of 14, mp 177 °C (mixture melting point), after recrystallization from a mixture (1:1) of methylene chloride and methanol.

III.4.9 Base-catalyzed Transformation of 13 to 15. To a stirred solution of the meso-isomer 13 (100 mg, 0.22 mmol)

in benzene (20 mL) was added triethylamine (100 mg, 1.0 mmol), and the stirring was continued for an additional period of 0.5 h. The solvent was removed under vacuum to give a residual solid which was chromatographed over silica gel. Elution with a mixture (1:2) of benzene and petroleum ether gave 25 mg (25%) of the unchanged starting material 13, mp 191-192 °C (mixture melting point), after recrystallization from 1:1 mixture of benzene and petroleum ether. On subsequent elution of the column with a mixture (1:1) of benzene and petroleum ether gave 55 mg (55%) of the d,l-butanedione 15, mp 182-183 °C (mixture melting point), after recrystallization from a 1:1 mixture of methylene chloride and petroleum ether.

III.4.10 Irradiation of Dimethyl 1-Benzotriazolylmaleate

(5) in Benzene. A benzene solution of 5 (500 mg, 1.914 mmol) was deaerated by purging with nitrogen and irradiated (RPR, 2537 Å) for 5.5 h. The solvent was removed under vacuum and the residue was chromatographed over silica gel. Elution with a mixture (1:9) of benzene and petroleum ether gave 25 mg (4%) of dimethyl 1-(2-phenylanilino)fumarate (16), mp 162-163 °C, after recrystallization from a mixture (1:2) of benzene and petroleum ether.

IR spectrum ν_{\max} (KBr): 3245 (ν_{NH}), 3090, 3045, 2995, 2968, 2882 and 2849 (ν_{CH}), 1740 and 1725 ($\nu_{\text{C=O}}$), 1635 and 1600 ($\nu_{\text{C=C}}$) cm^{-1} .

UV spectrum λ_{max} (methanol): 255 nm (ϵ , 18,940), and 339 (8,760).

^1H NMR spectrum (CDCl_3): δ 3.45 (s, 3 H, methoxy), 3.60 (s, 3 H, methoxy), 6.25 (s, 1 H, vinylic), 7.15-7.45 (m, 9 H, aromatic), and 8.15 (bs, 1 H, D_2O -exchangeable, NH).

Mass spectrum, m/e (relative intensity): 311 (M^+ , 2), 280 ($\text{M}^+ - \text{OCH}_3$, 4), 279 ($\text{M}^+ - \text{OCH}_3$, -H, 2), 252 ($\text{M}^+ - \text{CO}_2\text{CH}_3$, 70), 168 ($\text{C}_{12}\text{H}_{10}\text{N}^+$, 11), 153 ($\text{C}_{12}\text{H}_9^+$, 44), 91 (38), 59 (100), and other peaks.

Anal. Calcd for $\text{C}_{18}\text{H}_{17}\text{NO}_4$: C, 63.88; H, 6.46; N, 5.32.
Found: C, 63.59; H, 6.31; N, 5.47.

On subsequent elution of the column with a mixture (1:4) of benzene and petroleum ether gave 80 mg (16%) of the fumarate 6, mp 90-91 °C (mixture melting point), after recrystallization from a mixture (1:1) of benzene and petroleum ether.

Further elution of the column with a mixture (1:2) of benzene and petroleum ether gave 60 mg (12%) of the unchanged starting material 5, mp 97-98 °C (mixture melting point), after recrystallization from methanol.

The column was finally eluted with a mixture (1:1) of benzene and petroleum ether to give 220 mg (50%) of dimethyl indole-2,3-dicarboxylate (17), mp 110-111 °C (lit.¹¹ mp 112 °C) after recrystallization from a mixture (1:1) of methylene chloride and petroleum ether.

III.4.11 Irradiation of Dimethyl 1-Benzotriazolyl-fumarate (6). A benzene solution of 6 (500 mg, 1.94 mmol) was irradiated (RPR, 2537 Å) for 5.5 h and worked up by a similar procedure to give 20 mg (3%) of 16, mp 162-163 °C (mixture melting point), 90 mg (18%) of the unchanged starting material 6, mp 90-91 °C (mixture melting point), 30 mg (6%) of 5, mp 97-98 °C (mixture melting point) and 260 mg (58%) of the indoleedicarboxylate 17, mp 110-111 °C (mixture melting point).

III.4.12 Irradiation of (Z)-1-(3,5-Diphenyl-1H-1,2,4-triazolyl)-1,2-dibenzoyl-ethylene (9). A solution of 9 (500 mg, 1.1 mmol) in benzene (500 mL) was irradiated (RPR, 3000 Å) for 8 h and removed the solvent under vacuum to give a residual solid, which was chromatographed over silica gel. Elution with petroleum ether gave 25 mg (10%) of trans-1,2-dibenzoyl-ethylene (22a), mp 109 °C (mixture melting point), after recrystallization from a mixture (1:2) of benzene and petroleum ether.

Further elution with a mixture (1:1) of benzene and petroleum ether gave 200 mg (40%) of erythro-5,6-dibenzoyl-5,6-dihydro[1-a,5-b]-2-phenyl-1,2,4-triazoloisoquinoline (19a), mp 157-158 °C, after recrystallization from a mixture (1:1) of methylene chloride and petroleum ether.

IR spectrum ν_{\max} (KBr): 3080, 3055, 2937, and 2895 (ν_{CH}), 1685 ($\nu_{\text{C=O}}$), 1610 and 1600 ($\nu_{\text{C=C}}$), and 1478 ($\nu_{\text{C=N}}$) cm^{-1} .

UV spectrum λ_{max} (methanol): 216 nm (ϵ , 55,400), 247 (90,340), and 282 (53,130).

^{13}C NMR spectrum (CDCl_3): δ 60.98 (C-6), 77.11 (C-5), 124.73, 125.40, 125.61, 126.99, 127.34, 128.57, 128.79, 129.18, 129.86, 130.11, 130.90, 133.63, 134.14, 134.29, 135.68, 152.42, 162.99, 192.48 (C=O), and 195.87 (C=O).

Mass spectrum, m/e (relative intensity): 455 (M^+ , 48), 378 ($\text{M}^+ - \text{C}_6\text{H}_5$, 11), 350 ($\text{M}^+ - \text{COC}_6\text{H}_5$, 73), 349 ($\text{M}^+ - \text{COC}_6\text{H}_5$, -H, 21), 245 ($\text{M}^+ - 2\text{COC}_6\text{H}_5$, 19), 219 (23), 105 ($\text{C}_6\text{H}_5\text{CO}^+$, 100), and other peaks.

Anal. Calcd for $\text{C}_{30}\text{H}_{21}\text{N}_3\text{O}_2$: C, 79.12; H, 4.62; N, 9.23. Found: C, 78.78; H, 4.49; N, 9.41.

The column was finally eluted with benzene to give 90 mg (38%) of 3,5-diphenyl-1,2,4-triazole (7), mp 188-189 °C (mixture melting point).

In a repeat experiment, 9 (500 mg, 1.1 mmol) was irradiated in methanol (500 mL) for 8 h (RPR, 3000 Å) and was worked up by a similar procedure to give 15 mg (6%) of trans-1,2-dibenzoyl-1-methoxyethylene (22b), mp 107-108 °C (mixture melting point), 240 mg (48%) of the triazoloisoquinoline derivative 19a, mp 157-158 °C (mixture melting point), and 70 mg (28%) of 7, mp 188-189 °C (mixture melting point).

III.4.13 Irradiation of (E)-1-(3,5-Diphenyl-1H-1,2,4-triazolyl)-1,2-dibenzoyl-ethylene (8). A benzene solution of 8

(200 mg, 0.44 mmol, in 250 mL) was irradiated (RPR, 3000 Å), for 4.5 h and worked up by removal of the solvent under vacuum and chromatographing the residue over silica gel. Elution with petroleum ether gave 10 mg (10%) of 22a, mp 108-109 °C (mixture melting point), after recrystallization from methanol. Further elution with a mixture (1:1) of benzene and petroleum ether gave 75 mg (48%) of threo-5,6-dibenzoyl-5,6-dihydro[1-a,5-b]-2-phenyl-1,2,4-triazolo[4,3-b]quinoline (19b), mp 171-172 °C, after recrystallization from methanol.

IR spectrum, ν_{\max} (KBr): 3070, 3050, 2985, and 2865 (ν_{CH}), 1685 ($\nu_{\text{C=O}}$), 1595 and 1575 ($\nu_{\text{C=C}}$), 1480 ($\nu_{\text{C=N}}$) cm^{-1} .

UV spectrum λ_{\max} (methanol): 217 nm (ϵ , 51,230), 255 (83,450), and 285 (68,300).

Anal. Calcd for $\text{C}_{30}\text{H}_{21}\text{N}_3\text{O}_2$: C, 79.12; H, 4.62; N, 9.23. Found: C, 79.45; H, 4.41; N, 9.18.

Final elution of the column with a mixture (9:1) of benzene and ethyl acetate gave 45 mg (47%) of 3,5-diphenyl-1,2,3-triazole (7), mp 188-189 °C (mixture melting point), after recrystallization from 90% ethanol.

III.4.14 Crystallographic Analysis of 13.²⁰ Suitable crystals of 13 ($\text{C}_{28}\text{H}_{20}\text{N}_6\text{O}_2$) for X-ray diffraction studies were obtained by recrystallization from a mixture (1:1) of methanol and methylene chloride. Data collections were performed with Mo $\text{K}(\alpha)$ radiation ($\lambda = 0.71073 \text{ \AA}$) on an Enraf-Norius CAD₄ computer

controlled kappa axis diffractometer equipped with a graphite crystal, incident beam monochromator. The crystals have cell constants of $a = 27.999$ (7), $b = 10.421$ (2), $c = 25.118$ (5) Å, $\beta = 95.31$ (2) $^\circ$ and $V = 7297.17$ (49) Å³. For $Z = 12$ and $F.W. = 472.50$ the calculated density is 1.285 g/cm² and the observed density (flotation in CCl₄/hexanes) was 1.286 g/cm³. The space group was determined to be $C2/c$ (# 15). A total of 7120 reflections were collected, of which 5696 were unique and not systematically absent. The structure was solved by direct methods.

Using 500 reflections (minimum E of 1.75) and 6831 relationships, a total of 11 phase sets were produced. A total of 54 atoms were located from an E-map prepared from the phase set with probability statistics: absolute figure of merit = 1.07, residual = 19.39, and psi zero = 0.890. The model was corrected in succeeding difference Fourier syntheses. The oxygen atoms were assigned from the geometry of the emerging model. The nitrogen atoms were assigned from the isotropic temperature factors when all but the oxygen atoms were considered as carbons. The three unique half-molecules all indicated the same pattern of nitrogen atom positions. Hydrogen atoms were located and added to the structure factor calculations but their positions were refined. The structure was refined using full-matrix least-squares techniques where the function minimized was $\sum W (|F_o| - |F_c|)^2$ with $w = (\sigma F_o)^2$. The final cycle of refinement

included 217 variable parameters and converged (largest parameter shift was 0.01 times its esd) with unweighted and weighted agreement factors of $R_1 = 0.091$ and $R_2 = 0.102$. All calculations were performed on a VAX 11/730 computer using SDP = VAX.²¹

Figure III.3 is a computer generated perspective drawing of 13 from the final X-ray coordinates showing the relative stereochemistry. The crystal structure consists of discrete molecular units. With 12 molecules in the unit cell, there must be $1\frac{1}{2}$ molecules in the asymmetric unit and each asymmetric unit contains one molecule in a general position and a half-molecule near a 2-fold axis. The entire cell thus contains 8 molecules at general positions and 4 molecules on two-fold axis. The closest intermolecular contacts are the 3.30 Å between O_1 and C_{17} and between N_8 and C_2 . The dihedral angle at $C_{21}-C_7$ bond is $60.5 (7)^\circ$.

III.4.15 Laser Flash Photolysis.¹⁴ For pulse laser excitation, outputs were obtained from a UV 400 Molelectron Nitrogen laser (337.1 nm, 2-3 mJ, ~ 8 ns) or Lambda-Physik MSC 101 excimer laser (Xe-Cl) (308 nm, ≤ 40 mJ, defocussed, ~ 20 ns). The transient phenomena were studied using a kinetic spectrophotometer, described elsewhere.²² In experiments where a large number of laser shots were necessary, e.g., for wavelength-by-wavelength measurements of transient absorption spectra, a flow system was used in which the solutions for

photolysis were allowed to drain from a reservoir through a quartz cell of 3 mm path length.

III.4.16 Pulse Radiolysis.¹⁴ The pulse radiolysis experiments were carried out, employing 7 MeV electron pulses (5 ns) from the Notre Dame ARCO-LP-7 linear accelerator in the computer controlled apparatus, described elsewhere.²³

III.5 REFERENCES

- (1) B. A. R. C. Murty, C. V. Kumar, V. Dabral, P. K. Das and M. V. George, J. Org. Chem. 49, 4165-4171 (1984).
- (2) B. A. R. C. Murty, Ph.D. Thesis, Indian Institute of Technology, Kanpur, 1982.
- (3) C. V. Kumar, B. A. R. C. Murty, S. Lahiri, E. Chakacherry, J. C. Scalano and M. V. George, J. Org. Chem. 49, 4923-4929 (1984).
- (4) C. V. Kumar, Ph.D. Thesis, Indian Institute of Technology, Kanpur, 1981.
- (5) B. A. R. C. Murty, S. Pratapan, C. V. Kumar, P. K. Das and M. V. George, J. Org. Chem. 50, 2533-2538 (1985).
- (6) B. B. Lohray, C. V. Kumar, P. K. Das and M. V. George, J. Org. Chem. 49, 4647-4656 (1984).
- (7) B. B. Lohray, Ph.D. Thesis, Indian Institute of Technology, Kanpur, 1983.
- (8) R. Barik, C. V. Kumar, P. K. Das and M. V. George, J. Org. Chem. 50, 4309-4317 (1985).
- (9) R. Barik, K. Bhattacharyya, P. K. Das and M. V. George, J. Org. Chem. 51, 3420-3428 (1986).
- (10) For some examples of the chemical shift differences in meso- and d,l-isomers of butane derivatives, see (a) J. W. Emsley, J. Feeney and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Pergamon Press: Oxford, Vol. 2, pp. 690-691 (1966); (b) P. Schar, "Nuclear

Magnetic Resonance Spectroscopy," CRC Press, Inc.: Florida, Vol. 2, pp. 8-9 (1983).

- (11) E. H. Huntress, T. E. Lesslie and W. M. Hearon, J. Am. Chem. Soc. 78, 419-423 (1956).
- (12) For some examples of 1,2-dibenzoylalkene rearrangement, see (a) G. W. Griffin and E. O'Connell, J. Am. Chem. Soc. 84, 4148-4149 (1962); (b) H. E. Zimmerman, H. G. C. Dürr, R. G. Lewis and S. Braun, J. Am. Chem. Soc. 84, 4149-4150 (1962); (c) A. Padwa, D. Crumrine and A. Schubber, J. Am. Chem. Soc. 88, 3064-3069 (1966); (d) N. Sugiyama and C. Kashima, Bull. Chem. Soc. Jpn. 43, 1875-1877 (1970); (e) H. E. Zimmerman, H. G. C. Dürr, R. S. Givens and R. G. Lewis, J. Am. Chem. Soc. 89, 1863-1874 (1967); (f) S. Lahiri, V. Dabral, S. M. S. Chauhan, E. Chakachery, C. V. Kumar, J. C. Scaiano and M. V. George, J. Org. Chem. 45, 3782-3790 (1980).
- (13) For some examples of photoelimination of nitrogen from benzotriazoles, see (a) E. M. Durgess, R. Carithers and J. McCullagh, J. Am. Chem. Soc. 90, 1923-1924 (1968); (b) P. Flowerday and M. J. Perkins, J. Am. Chem. Soc. 91, 1035-1036 (1969); (c) J. H. Boyer and R. Selvarajan, J. Heterocycl. Chem. 6, 503-506 (1969); (d) M. Ohashi, K. Tsujimoto and T. Yonezawa, J. Chem. Soc. Chem. Commun. 1089-1090 (1970); (e) H. Meier and I. Menzel, Liebigs Ann. Chem. 739, 56-62 (1970); (f) P. Claus, Th. Doppler, N. Gakis, M. Georgarakis, H. Giezendanner, P. Gilgen,

- H. Heimgartner, B. Jackson, M. Markey, N. S. Narasimhan, H. J. Rosenkranz, A. Wunderli, H.-J. Hansen and H. Schmid, *Pure Appl. Chem.* 33, 339-361 (1973); (g) M. Markey, H. Schmid and H.-J. Hansen, *Helv. Chim. Acta*, 62, 2129-2153 (1979); (h) P. A. Wender and C. B. Cooper, *Tetrahedron*, 42, 2985-2991 (1986).
- (14) All laser flash photolysis and pulse radiolysis studies were carried out by Dr. P. K. Das, Dr. S. Rajadurai and Professor M. V. George at the Radiation Laboratory of the University of Notre Dame (USA).
- (15) G. Charrier and A. Berett, *Gazz. Chim. Ital.* 51(II), 267-269 (1921); *Chem. Abstr.* 16, 1069 (1922).
- (16) K. T. Potts, *J. Chem. Soc.* 54, 3461-3464 (1954).
- (17) R. E. Lutz and W. R. Smithey, *J. Org. Chem.* 16, 51-56 (1951).
- (18) R. E. Lutz, *Organic Synthesis*, A. H. Blatt Ed., John Wiley and Sons, Inc.: New York, Collect. Vol. 3, pp. 248-250 (1955).
- (19) E. H. Huntress, T. E. Lesslie and J. Bornstein, *Organic Synthesis*, N. Rabjohn Ed., John Wiley and Sons, Inc.: New York, Collect. Vol. 4, pp. 329-330 (1963).
- (20) The X-ray crystallographic analysis of 13 has been carried out by Dr. C. Eigenbrot of the Molecular Structure Facility, Department of Chemistry, University of Notre Dame (USA).
- (21) B.A. Frenz, "Computing in Crystallography," H. Schenk, R. Olthof-Hazelkamp, H. van Konigsveld and G. C. Bassi Eds.,

Delft University Press: Delft, Holland, pp. 64-71 (1978).

- (22) P. K. Das, M. V. Encinas, R. D. Small Jr., and J. C. Scaiano, *J. Am. Chem. Soc.* 101, 6965-6970 (1979); (b) P. K. Das and K. Bobrowski, *J. Chem. Soc. Faraday Trans. 2*, 77, 1009-1027 (1981); (c) S. K. Chattopadhyay, P. K. Das and G. Hug, *J. Am. Chem. Soc.* 104, 4507-4514 (1982); (d) V. Nagarajan and R. W. Fessenden, *J. Phy. Chem.* 89, 2330-2335 (1985).
- (23) L. K. Patterson and J. Lilie, *Int. J. Radiat. Phys. Chem.* 6, 129-141 (1974).

VITAE

Born on September 16, 1956, in Eram (Orissa). R. Barik had his early education at Eram and completed his schooling at S.M. High School (Eram) in 1975. He obtained the degree of Bachelor of Science from Bhadrak College, Bhadrak (Orissa) in 1979 and the degree of Master of Science from, Ravenshaw College, Cuttack under Utkal University, Bhubaneswar in 1981.

He joined the Ph.D. programme in the Department of Chemistry, Indian Institute of Technology, Kanpur in December 1981. Presently he is a Senior Research Fellow in the same Department.

CHP
66

5th Lot

CHM-1986-D-BAR-P110 WA 00010